

boxylates in the two axial positions; for Ca(2), a distorted pentagonal bipyramid with the bidentate carboxylate and four water molecules in equatorial positions and symmetry-related monodentate carboxylates axially disposed. The primary mode of bonding to the mellitate ring involves a four-membered chelate ring containing the calcium ion and both oxygen atoms of the carboxylate group. This mode of bonding is commonly found for calcium ion coordination to organic carboxylates; for example, it has previously been observed as the primary mode of calcium ion binding in calcium malate dihydrate,¹⁵ calcium fumarate trihydrate,¹⁶ and calcium terephthalate trihydrate.⁵ The interaction of Ca²⁺ with a benzenepoly-carboxylate containing ortho-related carboxylates (e.g., mellitate with two or less acid hydrogens¹⁷) might conceivably involve the formation of a seven-membered chelate ring containing Ca²⁺ and the two ortho-related carboxylates; this would require the rotation of the two carboxylates to suitable positions with a minimum of steric strain. Models can be constructed which indicate that the two carboxylates can be suitably placed without any restrictive steric interactions. However, evidence of such binding was not found in the structure of the Ca₂H₂mellitate crystal. We therefore prefer to believe that the four-membered ring formation involving the Ca²⁺ and a single carboxylate provides the most stable metal-ligand interaction in such a complex. The presence of seven-membered ring formation, of course, cannot be ruled out in aqueous solution and may well be involved as a (transition) state of binding in the rapidly exchanging Ca²⁺-ligand solution system.

To the best of our knowledge, only one other Ca²⁺-benzenecarboxylate (1:1) binding constant has been reported:¹⁸ Ca²⁺phthalate²⁻, log K_{11} = 1.07 (IS = 0.15). The significantly larger value of log K_{11} = 3.05 (IS = 0.10) for Ca²⁺mellitate⁶⁻ is not unexpected due to the higher charge of the anion and the presence of six carboxylates which are all equally available

for binding with Ca²⁺ in the course of the rapid exchange processes occurring in aqueous solution. Perhaps an even stronger interaction might be expected between Ca²⁺ and a highly charged ligand such as mellitate⁶⁻ (pK₆ = 7.49). However, this charge is evenly distributed over a relatively large, probably highly hydrated molecule; and, apparent from the structural analysis of Ca₂H₂mellitate, the effectiveness of this charge with respect to binding Ca²⁺ cannot be augmented by suitable chelation as, for example, in the calcium complex of EDTA⁴⁻¹⁹ which has a stability constant of log K = 10.6.²⁰ It is of interest to compare the stability of the Ca²⁺mellitate binding with that of Ca²⁺oxydiacetate²⁻ which has a very similar 1:1 stability constant (log K = 3.4).²¹ Relative to mellitate, the ODA anion is of considerably lower charge and contains fewer binding sites; however the stability of the CaODA complex is derived to a large degree from the ability to form two fused five-membered chelate rings involving both carboxylates and the ether oxygen atom.¹⁴ In view of the characteristics of the mellitate anion (e.g., high charge and multiple, separated binding sites), in solutions of relatively high Ca²⁺ concentration the presence of complexes with more than one Ca²⁺ per ligand is also to be expected. In fact, in order to suitably fit the calcium electrode titration data it was necessary to assume, in addition to the 1:1 complex, the presence of a complex of stoichiometry Ca₂(mellitate)²⁻ with a stability constant (K_{21} = 0.37 × 10³) of a magnitude not greatly different from the 1:1 complex.

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Supplementary Material Available: Listings of anisotropic thermal parameters (Table A-I), structure factor amplitudes (Table A-II), [Ca²⁺] vs. emf standard curve (Figure A-1), and titration data containing [Ca²⁺] and the average number of Ca²⁺ ions bound per ligand (Table A-III) (16 pages). Ordering information is given on any current masthead page.

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Bis(dithiocarbamato)-Nitrosyl Complexes of Ruthenium

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The synthesis of new dithiocarbamato complexes of ruthenium is reported including *trans*-[RuNO(S₂CNRR')₂Cl] (R = R' = Me, Et; R = Me, R' = Et; R = Me, R' = Ph), *trans*-[RuNO(S₂CNMe₂)₂OH]·CH₃OH, *trans*-[RuNO(S₂CNMe₂)₂H₂O]BF₄, *trans*-[RuNO(S₂CNMe₂)₂CH₃OH]PF₆, *cis*-[RuNO(S₂CNMe₂)₂X] (X = F, Br, I, NO₂), *cis*-[RuNO(S₂CNRR')₂X] (X = Br, I; R = R' = Et; R = Me, R' = Et), and *cis*- and *trans*-[RuNO(S₂CNMe₂)₂X] (X = N₃, SCN, NCO). In contrast with the iron complex, *cis*-Ru(NO)(¹⁵NO₂)(S₂CNMe₂)₂ does not undergo exchange between the NO and NO₂ ligands. The spectral characteristics of these complexes are discussed in relation to their geometric configuration. The ¹³C NMR spectra of many of these complexes are reported and give valuable information regarding the bound ligand. The rotation of the unidentate dithiocarbamate ligand in *cis*-[RuNO(S₂CNMe₂)₂] is clearly differentiated from the two bidentate ligands.

Introduction

Sulfur ligands stabilize numerous nitrosyl complexes, but few sulfur derivatives of ruthenium nitrosyls have been reported. Those ruthenium complexes which are known include *cis*-Ru(NO)(S₂CNR₂)₃ (R = Me, Et),^{1,2} *trans*-Ru(NO)-

(Cl)(SacSac)₂,³ RuX₃(NO)L₂ (X = Cl, Br; L = Me₂S, Et₂S, PhEtS, PhMeS, (*n*-Pr)₂S, *n*-PrPhS),⁴ and [RuBr₃(NO)-

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Table I. Properties of Nitrosyl-Dithiocarbamate Complexes of Ruthenium

complex	color	mp, °C dec	Λ_m , S cm ² ^a
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ Cl]	yellow	316-318	
<i>trans</i> -[RuNO(S ₂ CNEt ₂) ₂ Cl]	yellow	187-189	2.6
<i>trans</i> -[RuNO(S ₂ CNMePh) ₂ Cl]	yellow	227-229	
<i>trans</i> -[RuNO(S ₂ CNMeEt) ₂ Cl]	yellow	246-248	1.7
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ N ₃]	yellow-orange	233-234	
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ NCO]	yellow	268-270	
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ SCN]	yellow	250-252	
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ OH]·CH ₃ OH	amber	224-228	2.4
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ H ₂ O]BF ₄	yellow	178-180	76 ^b
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ CH ₃ OH]PF ₆	yellow	134-137 ^f	60
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂]	deep red	218-220	0.3
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ F]	brown	130-135 ^f	17 ^h
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ Br]	gold-brown	248-249	3.9
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ I]	black-brown	283-287	4.2
<i>cis</i> -[RuNO(S ₂ CNEt ₂) ₂ Br]	brown	122-126	
<i>cis</i> -[RuNO(S ₂ CNEt ₂) ₂ I]	black-brown	132-135	
<i>cis</i> -[RuNO(S ₂ CNMeEt) ₂ Br]	brown	150-155	
<i>cis</i> -[RuNO(S ₂ CNMeEt) ₂ I]	brown	146-149	
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ NO ₂] ^{1/4} ·CH ₃ OH	light brown	200-202	4.3
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ N ₃]	light brown	232-233 ^d	4.7
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ SCN]	brown	250-252 ^d	3.0
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ NCO]	khaki	271-273 ^d	
BP ^e	brown	209-214	3.6 ^c (465 ^g)

^a In CH₃NO₂; 1:1 complexes; Λ_m ~75-90 S cm². ^b In CH₃OH; 1:1 complexes; Λ_m ~80-115 S cm². ^c In DMF, 1:1 complexes; Λ_m ~65-90 S cm². ^d Isomerization to *trans* complex occurs. ^e Mixture of *cis*-[RuNO(Me₂NCS)₂] and *trans*-[RuNO(OH)(Me₂NCS)₂] in 2:1 ratio. ^f Impure complexes. ^g Molecular weight measured in CHCl₃ and extrapolated to zero concentration (concentration range 4.8-31.5 mg/mL). ^h Λ_m consistent with presence of aquo and methanol complexes.

(Et₂SO)]₂.⁵ In addition to these nitrosyl species, Ru^{III}(S₂CNR₂)₃,^{6,7} Ru(CO)₂(S₂CNR₂)₂ (R = Me, Et, C₆H₅CH₂),⁸ Ru(CO)(S₂CNR₂)₂ (R = Me, Et),⁸ [Ru^{III}(S₂CN(CH₂Ph)₂)(CO)₂Cl]₂,⁸ and [Ru₂(S₂CNEt₂)₅]BF₄⁹ and the seven-coordinate complexes of ruthenium(IV) RuCl(S₂CNEt₂)₃¹⁰ and Ru(S₂CNMe₂)₃I₃¹¹ have been reported. More recently the chemical and electrochemical properties of new ruthenium(II), -(III), and -(IV) dithiocarbamate complexes have been described.¹² The related series of iron nitrosyl complexes Fe(NO)(S₂CNR₂)₂ (R = Me, Et, Ph),^{13,14} Fe(NO)(S₂CNMe₂)₂X (X = Br, I, NO₂, SCN), and [Fe(NO)(S₂CNMe₂)₂X]Y (X = CH₃CN, CH₃NC, C₅H₅N; Y = BF₄, PF₆)¹⁴ have been prepared and their reactions investigated. The observation^{14,15} that *cis*-Fe(NO)(S₂CNMe₂)₂(NO₂) undergoes a novel intramolecular oxygen exchange between the coordinated nitro and nitrosyl groups has prompted the present investigation.

Results

Synthesis and Reactions. The reaction between ruthenium nitrosyl trichloride and 2 equiv of dithiocarbamate ligand

resulted in the exclusive formation of the *trans* isomers, *trans*-Ru(NO)(S₂CNRR')₂Cl (where R = R' = Me or Et; R' = Et or Ph). Treatment of ruthenium nitrosyl trichloride in methanol with 3 equiv of sodium dimethyldithiocarbamate led to the formation of a less tractable brown material. Although this brown material was obtained consistently from this reaction, it is a mixture of Ru(NO)(S₂CNMe₂)₃ and *trans*-Ru(NO)(S₂CNMe₂)₂(OH). The two components of this mixture were separated by chromatography and identified by comparison of their NMR spectra with authentic samples independently prepared. Refluxing this brown mixture or ruthenium nitrosyl trichloride with *excess* sodium dimethyldithiocarbamate resulted in the formation of deep red crystals of Ru(NO)(S₂CNMe₂)₃, a complex which has been prepared previously from the reaction of NO with Ru(S₂CNMe₂)₃.^{1,2} This brown mixture also reacts with HF, HBr, and HI but not with H₂S to form the corresponding *cis*-Ru(NO)(S₂CNMe₂)₂X complexes. However, except for the fluoro derivative, the other synthetic routes described below are superior. In this reaction, the fluoro complex was obtained in low yields and was accompanied by varying amounts of the aquo complex.

Reaction of any of the *trans* chloride complexes with HBr or HI produced the corresponding bromide or iodide complexes with *cis* geometry. Other derivatives with *cis* configurations were prepared by treatment of either *cis*-Ru(NO)(S₂CNMe₂)₂I or *trans*-Ru(NO)Cl(S₂CNMe₂)₂ in methanol with AgX (where X = N₃, NCO, or NCS). Some *trans*-Ru(NO)(S₂CNMe₂)₂(OH) was also formed in these reactions with AgX and was identified by direct preparation from the reaction of Ag₂O with *cis*-Ru(NO)(S₂CNMe₂)₂I. To obtain analytically pure materials, it was found necessary to purify each of these compounds by column chromatography.

In an attempt to isolate both *cis* and *trans* isomers of individual complexes, several solvates were prepared from *cis*-Ru(NO)(S₂CNMe₂)₂I or *trans*-Ru(NO)Cl(S₂CNMe₂)₂ by using AgBF₄ or AgPF₆. These compounds include *cis*-[Ru(NO)(S₂CNMe₂)₂(MeOH)] [PF₆], *trans*-[Ru(NO)(S₂CNMe₂)₂(H₂O)] [BF₄], and [Ru(NO)(S₂CNMe₂)₂(MeOH)] [PF₆]. Although this approach had limited success in that both *cis* and *trans* isomers of the azido, cyanato, and

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Table II. Analytical Results (Experimental Values in Parentheses)

complex	% C	% H	% N	% X	% O
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ Cl]	17.71 (17.65)	2.97 (2.70)	10.32 (10.23)	8.71 (9.00)	
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ Cl]	25.94 (25.45)	4.35 (4.06)	9.08 (8.91)	7.66 (7.70)	
<i>trans</i> -[RuNO(S ₂ CNMePh) ₂ Cl]	36.18 (35.98)	3.04 (2.91)	7.91 (7.85)	6.67 (6.60)	
<i>trans</i> -[RuNO(S ₂ CNMeEt) ₂ Cl]	22.09 (21.86)	3.71 (3.54)	9.66 (9.45)	8.15 (8.23)	
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ N ₃]	17.43 (17.43)	2.93 (2.78)	20.32 (20.12)		
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ NCO]	20.33 (20.45)	2.93 (3.17)	13.55 (13.39)		
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ SCN]	19.57 (19.64)	2.82 (2.66)	13.04 (12.87)		
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ OH]·CH ₃ OH	19.99 (19.95)	4.08 (3.70)	9.99 (9.97)		11.41 (10.59)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ H ₂ O]BF ₄	15.13 (15.09)	2.96 (3.30)	8.82 (8.55)		
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ CH ₃ OH]PF ₆	15.33 (14.20)	2.94 (3.02)	7.66 (7.19)		
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂]	21.98 (22.03)	3.69 (3.57)	11.39 (11.14)		
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ F]	18.45 (19.00)	3.10 (2.81)	10.76 (10.18)	4.87 (4.14)	
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ Br]	15.96 (16.06)	2.68 (2.55)	9.31 (9.18)	17.70 (18.00)	
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ I]	14.46 (14.63)	2.43 (2.21)	8.43 (8.19)	25.46 (25.37)	
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ Br]	23.67 (23.88)	3.97 (3.72)	8.28 (8.55)	15.74 (16.00)	
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ I]	21.66 (21.68)	3.64 (3.49)	7.58 (7.39)	22.89 (23.06)	
<i>cis</i> -[RuNO(S ₂ CNMeEt) ₂ Br]	20.04 (20.19)	3.36 (3.15)	8.76 (8.66)	16.67 (16.90)	
<i>cis</i> -[RuNO(S ₂ CNMeEt) ₂ I]	18.25 (18.51)	3.06 (2.88)	7.98 (7.70)	24.10 (24.30)	
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ NO ₂]·1/4 CH ₃ OH	17.64 (17.59)	3.08 (2.77)	13.17 (13.09)		12.22 (12.33)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ N ₃]	17.43 (17.70)	2.93 (2.87)	20.32 (20.27)		
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ SCN]	19.57 (19.84)	2.82 (2.56)	13.04 (12.82)		
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ NCO]	20.33 (20.59)	2.93 (2.68)	13.55 (13.27)		
NaS ₂ CNMeEt·3H ₂ O	22.74 (22.49)	6.68 (5.97)	6.63 (6.37)		
Bp ^a	21.01 (21.39)	3.60 (3.36)	11.23 (10.91)		4.67 (4.56)

^a *cis*-[RuNO(S₂CNMe₂)₂] + *trans*-[RuNO(S₂CNMe₂)₂OH] (2:1).

thiocyanato complexes were isolated, this synthetic route normally led to mixtures of *cis* and *trans* isomers which had to be separated by column chromatography. An unusual and superior synthetic route for conversion of *cis* isomers to *trans* was fortunately discovered, however. Heating the solid *cis* azido, cyanato, and thiocyanato complexes in the temperature range from 160 to 210 °C resulted in rapid and quantitative conversion of the *trans* isomers to *cis* geometry as judged by infrared and NMR spectroscopy and by microanalysis. Some properties of the 22 isomerically pure compounds prepared in this study are listed in Table I. Their elemental analyses are set out in Table II.

One of the primary aims in this research was to explore the possible exchange reaction between NO and NO₂ ligands bound to ruthenium. Consequently, the ¹⁵N-enriched and unenriched nitro complex *cis*-Ru(NO)(S₂CNMe₂)₂(NO₂) was prepared from the reaction of *cis*-Ru(NO)(S₂CNMe₂)₂I with Ag¹⁵NO₂ and AgNO₂, respectively. Neither nitrito complexes nor the *trans* isomer was observed in these reactions. The oxygen atom transfer reaction reported for *cis*-Fe(NO)(S₂CNMe₂)₂(NO₂)¹⁴ was explored for the ¹⁵N-labeled ruthenium complex. Even though the NO and NO₂ ligands occupy adjacent coordination sites in *cis*-Ru(NO)(S₂CNMe₂)₂(¹⁵NO₂), the nitrosyl ligand maintained its isotopic integrity under all of the experimental conditions to which it was subjected. Refluxing the *cis* nitro complex in toluene for 8 h did not result in ¹⁵N enrichment of the nitrosyl ligand. Photolysis in dichloromethane resulted only in the loss of the coordinated ¹⁵NO₂ ligand. Exchange was also not effected by the addition of Fe(NO)(S₂CNMe₂)₂ to solutions of the labeled ruthenium complex.

The lowered reactivity of these ruthenium complexes compared with the iron complexes was not unexpected, since it is well-known that ruthenium complexes are kinetically more inert than iron complexes. Moreover, the {RuNO}⁶ species are among the most stable nitrosyl complexes which are known. However, {RuNO}⁶ do readily react with nucleophiles,¹⁶ so that attack by the adjacent oxygen of the NO₂ ligand is not unreasonable. Neither the addition of a radical initiator (Fe(NO)(S₂CNMe₂)₂) nor photolysis led to oxygen atom ex-

change, however, indicating that the necessary activated complex is probably inaccessible.

Infrared Spectra. The solid-state spectra contained a number of intense absorption bands arising principally from $\nu(\text{NO})$, $\nu(\text{CN})$, and certain vibrations of several substituted ligands (Table III). The nitrosyl stretching frequencies occurred in the range 1795–1870 cm⁻¹. Splitting of $\nu(\text{NO})$ was observed in a few cases and was attributed to crystal lattice effects since solutions of these complexes exhibited only a single nitrosyl absorption band. The value of $\nu(\text{NO})$ for the *trans* isomer was approximately 20 cm⁻¹ higher than that of the *cis* isomer for the series [RuNO(S₂CNMe₂)₂X] (X = N₃, NCO, NCS). Appreciable variation in $\nu(\text{NO})$ occurred among the *trans* isomers, ranging from 1795 cm⁻¹ for the hydroxo complex to 1870 cm⁻¹ for the methanol species. These variations reflect the differing *trans* influences of the substituents. Sinitsyn and Zvyagintsev¹⁶ reported the effects of the *trans* ligand upon $\nu(\text{NO})$ and assumed that this was directly related to the strength of the Ru–NO bond. Later, Mercer et al.¹⁷ broadened this study by examining the effect of the *trans* ligand upon $\nu(\text{Ru–NO})$ in the series *cis*- and *trans*-[RuNO(X)(NH₃)₄]²⁺.

The $\delta(\text{Ru–NO})$ and $\nu(\text{Ru–NO})$ absorptions are usually weak^{18,19} and no assignments were made. Since $\nu(\text{Ru–NO})$ could not be assigned with certainty, $\nu(\text{NO})$ was taken as the measure of the effect exerted by the *trans* ligand. For the dimethyldithiocarbamato complexes, the hydroxide ion had the strongest *trans* effect and methanol the weakest. The variation of $\nu(\text{NO})$ with *trans* substituent was in general agreement with the trends previously reported.^{16,17} In contrast the *cis* complexes showed little variation in $\nu(\text{NO})$ since the ligand *trans* to NO is a dithiocarbamate sulfur atom in each case. Similar results have also been noted for *cis*-RuNO(X)(AA)₂ (X = Cl, Br; AA = bpy, phen),²⁰ although a *cis* effect has been reported for other ruthenium nitrosyl complexes.^{17,20}

The $\nu(\text{CN})$ frequency of these complexes at ca. 1540 cm⁻¹ is nearly independent of the substituent. It is shifted to higher

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Table III. Infrared Spectra (cm^{-1}) of $[\text{RuNO}(\text{S}_2\text{CNRR}')_2\text{X}]$ and $[\text{RuNO}(\text{S}_2\text{CNRR}')_2\text{X}]\text{Y}$ (KBr Pellets)^a

complex	$\nu(\text{NO})$	$\nu(\text{CN})$	bands due to	
			X	Y
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{Cl}]$	1825 s 1805 ms, sp (1845) ^b	1540 s		
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{Cl}]$	1840 s	1510 s		
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMePh})_2\text{Cl}]$	1835 s	1490 s		
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{Cl}]$	1835 s 1805 sh (1840) ^b	1530		
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{N}_3]$	1820 s 1800 sh (1840) ^b	1540 s	2050 s $\nu_a(\text{N}_3)$ 1290 w $\nu_s(\text{N}_3)$	
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{NCO}]$	1820 s 1805 ms, sp (1845) ^b	1530	2110 s $\nu_a(\text{NCO})$ 1350 m, sp $\nu_s(\text{NCO})$ 595 m $\delta(\text{NCO})$	
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{SCN}]$	1840 s	1540 s	2065 s $\nu(\text{CN})$ 2090 s	
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{OH}]\cdot\text{CH}_3\text{OH}$	1795 s	1530 s	3500 m, br $\nu(\text{OH})$ 2785 m, sp $\nu(\text{OH})$ 1070 ms $\delta(\text{Ru-OH})$ 475 m $\nu(\text{Ru-OH})$	
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{H}_2\text{O}]\text{BF}_4$	1810 s	1540 s	3150 sh 3300 br, ms $\nu(\text{OH})$ 3400 sh 3500 sh	1030 s 1060 s 1100 s
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{CH}_3\text{OH}]\text{PF}_6$	1870 s	1550 s	1610 br, w $\delta(\text{HOH})$ 3600 sh $\nu(\text{OH})$ 3450 ms, br 1650 sh $\delta(\text{OH})$ 1000 w 485 w	840 560 s
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_3]$	1825 s	1535 s 1490 ms, sh		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{F}]$	1800 s	1540 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{Br}]$	1810 s	1540 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{I}]$	1805 s	1535 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{Br}]$	1810 s	1525 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{I}]$	1800 s	1510 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{Br}]$	1800 s	1520 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{I}]$	1800 s	1520 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{NO}_2]\cdot\frac{1}{4}\text{CH}_3\text{OH}$	1805 s	1545 s	1310 s $\nu_s(\text{NO}_2)$ 820 ms, sp $\delta(\text{NO}_2)$ 1360 s $\nu_a(^{15}\text{NO}_2)$ 1290 s $\nu_s(^{15}\text{NO}_2)$ 815 ms, sp $\delta(^{15}\text{NO}_2)$	
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2^{15}\text{NO}_2]$	1805 s	1545 s	1995 s $\nu_a(\text{N}_3)$ 2010 s, sh $\nu_s(\text{N}_3)$ 1275 m $\nu_s(\text{N}_3)$ 2100 s $\nu(\text{CN})$ 2175 s $\nu_a(\text{NCO})$ 2200 sh $\nu_s(\text{NCO})$ 1320 w $\nu_s(\text{NCO})$ 2760 m, sp $\nu(\text{OH})$ 1070 m $\delta(\text{Ru-OH})$ 480 w $\nu(\text{Ru-OH})$	
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{N}_3]$	1800 s	1540 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{SCN}]$	1825 s	1550 s		
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{NCO}]$	1800 s	1535 s		
BP ^c	1800 s	1535 s 1480 sh		

^a Abbreviations used: br = broad, m = medium, ms = medium strong, s = strong, sh = shoulder, sp = sharp, w = weak. ^b Measured in CH_2Cl_2 . ^c Mixture of *cis*- $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_3]$ and *trans*- $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{OH}]$.

energy compared with the free ligand as a result of increased double-bond character upon coordination to the metal center.^{22,23} The shoulder observed at 1480 cm^{-1} in *cis*- $\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_3$ was attributed to the unidentate dithiocarbamate ligand.

Various coordinating substituents produced characteristic absorption bands. The isomers of $\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{X}$ ($\text{X} = \text{N}_3$, NCO , NCS) revealed prominent $\nu_a(\text{N}_3)$, $\nu_a(\text{NCO})$, and $\nu(\text{CN})$ absorptions between 2210 and 2000 cm^{-1} . However $\nu_s(\text{N}_3)$ and $\nu_s(\text{NCO})$ were much weaker, and $\nu(\text{CS})$ was not observed. Both the *trans* azido and cyanato complexes pos-

sessed higher ν_a and ν_s stretching frequencies than their *cis* analogues while the reverse was true for $\nu(\text{CN})$ of the corresponding thiocyanato complexes. The value of $\nu(\text{CN})$ suggested S coordination by the SCN ligand.²⁴ The bands above 1350 cm^{-1} in the isocyanato complexes are higher than ν_s of free NCO^- and indicate N coordination by the ligand.²⁴ Isomerization of *cis*- $\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{X}$ ($\text{X} = \text{N}_3$, NCO , NCS) to the *trans* isomers resulted in the loss of the $\nu(\text{NO})$ and $\nu(\text{X})$ vibrations of the *cis* isomers and the appearance of $\nu(\text{NO})$ and $\nu(\text{X})$ of the *trans* isomers.

Two of the three NO_2 vibrations of the nitro complex were observed at 1310 cm^{-1} ($\nu_s(\text{NO}_2)$) and 820 cm^{-1} ($\delta(\text{NO}_2)$). In

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Table IV. ^1H NMR Absorptions of $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{X}]$ (in CDCl_3) Relative to Me_4Si (Ppm)^a

complex	$-\text{CH}_3$	$-\text{CH}_2-$	$-\text{C}_6\text{H}_5$	X	integratn
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{Cl}]$	3.34				
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{Cl}]$	1.43, 1.33, 1.23	3.95, 3.93, 3.83 3.80, 3.70, 3.67, 3.57			$\text{CH}_3:\text{CH}_2 = 1.6:1$
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMePh})_2\text{Cl}]$	3.67		7.42		$\text{C}_6\text{H}_5:\text{CH}_3 = 1.8:1$
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{Cl}]$	1.23, 1.37, 1.48 3.33	3.60, 3.67, 3.72 3.77, 3.83, 3.92, 4.03			$\text{CH}_3:\text{CH}_2 = 3.1:1$
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{N}_3]$	3.36				
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{NCO}]$	3.36				
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{SCN}]$	3.35				
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{OH}]\cdot\text{CH}_3\text{OH}$	3.37			4.02 br s (OH)	
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{H}_2\text{O}]\text{BF}_4^b$	3.50			3.18 br (H_2O)	
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{CH}_3\text{OH}]\text{PF}_6^b$	3.52			3.32 CH_3 , 3.17 br (OH)	$\text{Me}_2\text{NCS}_2:\text{MeOH} = 4.1:1$ $\text{A}:\text{B} = 2.0:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_3]$	3.22, 3.35, 3.38 (A) 3.58 (B)				$\text{A}:\text{B} = 3:1$
BP^c	3.20, 3.34, 3.37 (A) 3.58 (B)				$\text{A}:\text{B} = 3:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{F}]$	3.38, 3.35 (A) 3.23 (B)				$\text{A}:\text{B} = 3:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{Br}]$	3.33, 3.28 (A) 3.22 (B)				$\text{A}:\text{B} = 3.1:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{I}]$	3.35, 3.32, 3.27 (A) 3.23 (B)				$\text{A}:\text{B} = 3.1:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{Br}]$	1.48, 1.45, 1.35	complex multiplet-broadened 3.82, 3.72, 3.67 3.58, 3.53, 3.47			$\text{CH}_3:\text{CH}_2 = 1.7:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{I}]$	1.33, 1.25, 1.20, 1.13 1.47, 1.42, 1.33, 1.30 1.22, 1.18, 1.10	complex multiplet 3.88, 3.82, 3.77 3.67, 3.65, 3.55, 3.43			$\text{CH}_3:\text{CH}_2 = 1.6:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{Br}]$	3.30, 3.27, 3.20 1.57, 1.43, 1.37, 1.32 1.25, 1.20, 1.13	complex multiplet 3.98, 3.87, 3.73 3.62, 3.50			$\text{CH}_3:\text{CH}_2\text{CH}_2 = 1:1.7$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{I}]$	3.30, 3.27, 3.25, 3.20 1.43, 1.37, 1.32, 1.22 1.20, 1.18, 1.12	complex multiplet 3.85, 3.73 3.62, 3.45			$\text{CH}_3:\text{CH}_2\text{CH}_2 = 1:1.8$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{NO}_2]\cdot\frac{1}{4}\text{CH}_3\text{OH}$	3.37, 3.35, 3.31 (A) 3.24 (B)				$\text{A}:\text{B} = 3.2:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{N}_3]$	3.37, 3.36 (A) 3.24 (B)				$\text{A}:\text{B} = 3.0:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{SCN}]$	3.37, 3.33, 3.30 (A) 3.19 (B)				$\text{A}:\text{B} = 2.8:1$
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{NCO}]$	3.35, 3.33 (A) 3.23 (B)				$\text{A}:\text{B} = 3.1:1$

^a For *cis*- $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{X}]$, A:B refers to the ratio of the integrated intensities of peaks at lower field (A) to that of the peak at highest field (B). ^b CD_3COCD_3 . ^c *cis*- $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_3]$ and *trans*- $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{OH}]$ in 2:1 ratio.

the ^{15}N labeled complex, ν_a was found at 1360 cm^{-1} . The observed NO_2 frequencies are indicative of N coordination by the nitro ligand.²⁴

The hydroxo, aquo, and methanol complexes had characteristic OH frequencies. The hydroxo complex was characterized by a sharp peak at 2785 cm^{-1} , probably associated with hydrogen bonding to methanol, a strong $\delta(\text{Ru}-\text{OH})$ band at 1070 cm^{-1} and a band at 475 cm^{-1} due to $\nu(\text{Ru}-\text{OH})$. In *trans*- $[\text{RuNO}(\text{OH})(\text{NH}_3)_4]\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\delta(\text{Ru}-\text{OH})$ and $\nu(\text{Ru}-\text{OH})$ occur at approximately 965 and 560 cm^{-1} , respectively.¹⁷ The aquo complex produced broad bands at approximately 3300 and 1610 cm^{-1} , due to asymmetric and symmetric $\nu(\text{OH})$ and $\delta_a(\text{HOH})$, respectively. The methanol complex produced absorptions similar to the aquo complex consistent with the spectra reported for several ethanol complexes prepared by Van Leeuwen.²⁵ The three weak bands at 1080 , 1000 , and 490 cm^{-1} were not assigned. If the solvent was not dried, the methanol complex was often found to be contaminated by the aquo species and the hydroxo complex resulting in an extra nitrosyl absorption near 1810 cm^{-1} . In view of these facts, the bands at 1080 and 490 cm^{-1} were attributed to the hydroxo complex, while that at 1000 cm^{-1}

was due to coordinated methanol.

NMR Spectra. The ^1H NMR spectra (Table IV) of the *trans* dimethyldithiocarbamato complexes produced a single sharp signal, indicating the equivalence of the methyl groups. A triplet and quartet were observed for *trans*- $\text{Ru}(\text{NO})\text{Cl}(\text{S}_2\text{CNEt}_2)_2$. In addition to the single CH_3 peak, the spectrum of *trans*- $\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_2(\text{OH})\cdot\text{CH}_3\text{OH}$ has a slightly broadened resonance at 4.02 ppm due to the OH groups. The CH_3 group of the solvate molecule was not observed in the ^1H NMR spectrum but was found in the ^{13}C NMR spectrum (vide infra). The aquo complex produced a broad peak at 3.18 ppm due to coordinated water. Addition of HBF_4 to solutions of the hydroxo complex resulted in new peaks at 3.50 and 3.18 ppm , indicative of conversion to the aquo complex. Two signals in the ratio of 4:1 corresponding to the dithiocarbamato and methanol methyl groups of *trans*- $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{CH}_3\text{OH}]^+$ were observed at 3.52 and 3.32 ppm . A broad peak at 3.17 ppm was attributed to the OH group of CH_3OH .

The *cis* dimethyldithiocarbamato complexes showed a maximum of four resonances in the ^1H NMR spectra, due to four inequivalent methyl groups. In those cases where only three signals were observed for *cis*- $\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{X}$ ($\text{X} = \text{F}, \text{Br}, \text{N}_3, \text{NCO}$), the resonances at lowest field were approximately twice the intensity of each of the other two. The

Table V. ^{13}C NMR Absorptions Relative to Me_4Si (Ppm)

compd	assignment				solvent
	$-\text{CH}_3$	$-\text{CH}_2$	$-\text{C} \begin{smallmatrix} \diagup \diagdown \\ \diagup \diagdown \end{smallmatrix}$		
$\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$	45.1		211.6		CD_3OD
	45.8		208.1		D_2O
$\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$	12.4	49.5	206.5		D_2O
$\text{NaS}_2\text{CNMeEt} \cdot 3\text{H}_2\text{O}$	43.0, 11.9	52.5	207.3		D_2O
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{Cl}]$	12.5	45.3	211.7		CDCl_3
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{Cl}]$	37.0, 11.9	47.6	212.1		CDCl_3
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{OH}] \cdot \text{CH}_3\text{OH}$	39.5, 53.4 (CH_3OH)		214.2		CDCl_3
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{N}_3]$	39.8		213.3		CDCl_3
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{SCN}]$	39.8		<i>a</i>		CDCl_3
<i>trans</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{H}_2\text{O}]\text{BF}_4$	40.6		210.3		CD_2COCD_3
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{NO}_2] \cdot 1/4 \text{CH}_3\text{OH}$	40.1, 39.7, 39.1		208.3, 203.3		CDCl_3
	38.3, 53.4 (CH_3OH)				
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{I}]$	36.7, 36.1, 35.9, 35.4	47.3, 46.4	210.4, 202.1		CDCl_3
	12.2, 12.0	45.6			
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNEt}_2)_2\text{I}]$	12.7, 12.5	44.9, 44.2, 43.4	210.0, 201.7		CDCl_3
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{I}]$	39.2, 38.6, 38.5, 37.9		211.1, 202.7		CDCl_3
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{Br}]$	39.3, 38.9, 38.8, 38.1		210.4, 203.4		CDCl_3
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{F}]^b$	46.9, 39.6, 39.3, 38.9, 38.4, 38.1		208.5, 202.1		CDCl_3
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{SCN}]$	39.5, 39.2, 39.0, 38.2		<i>a</i>		CDCl_3
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{N}_3]$	39.8, 39.4, 39.0, 38.2		210.4, 204.3		CDCl_3
<i>cis</i> - $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_3]$	45.8, 44.3 br		210.9, 205.9		CDCl_3
	39.4, 39.1, 39.0, 38.2		203.9		
BP	45.9, 44.5 br		214.2, 210.6		CDCl_3
	39.5, 39.3, 39.0		205.7, 203.7		
	38.9, 38.1				
<i>cis</i> - $[\text{FeNO}(\text{S}_2\text{CNMe}_2)_2\text{NO}_2]$	39.5, 38.9, 38.5, 37.9		204.0, 202.2		CDCl_3

^a Quaternary carbon resonances not observed. ^b Peaks due to methanol and to aquo complex also present.

spectra of the *cis* complexes indicated that at ambient temperature the dithiocarbamate ligand is essentially stereochemically rigid. The result of isomerizing *cis*- $\text{RuNO}(\text{S}_2\text{CNMe}_2)_2\text{X}$ ($\text{X} = \text{N}_3, \text{NCO}, \text{NCS}$) to the *trans* isomer was clearly evident in the ^1H and ^{13}C NMR spectra. The multiple methyl resonances of the *cis* isomers changed to a single peak indicative of the *trans* complexes. The ^1H NMR spectrum of *cis*- $[\text{RuNO}(\text{S}_2\text{CNMe}_2)_3]$ produced a strong signal at 3.58 ppm of half the area of the methyl resonances at higher field and was attributed to the methyl groups of the unidentate dithiocarbamate ligand.

The proton-decoupled ^{13}C NMR spectra (Table V) substantiated the isomeric assignments made from ^1H NMR and confirmed the stereochemical rigidity of the bidentate dithiocarbamate ligand at ambient temperatures. Single ^{13}C resonances were observed for the methyl, methylene, and quaternary carbons of the *trans* complexes. Being unenhanced by NOE, the signals of the quaternary carbons were much weaker than those of the other carbon atoms and consequently were more difficult to detect. However, in the presence of a paramagnetic species the T_1 relaxation time of quaternary carbon nuclei is decreased,²⁶⁻²⁸ allowing detection without recourse to long pulse delays or very small flip angles. With $\sim 0.1 \text{ mol dm}^{-3}$ of $\text{Cr}^{\text{III}}(\text{acac})_3$, significant enhancement of signal intensities was obtained with no observable contact shift ($< 0.1 \text{ ppm}$) and only modest line broadening. The poor solubility of *cis*- and *trans*- $\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_2(\text{SCN})$ prevented observation of the quaternary carbon resonances even in the presence of chromium(III).

The *cis* dimethyldithiocarbamate complexes produced four methyl and two quaternary carbon peaks in each case. The spectrum of the fluoro complex showed three extra peaks which were due to the presence of the aquo and methanol impurities.

The spectrum of *cis*- $\text{RuNO}(\text{S}_2\text{CNMe}_2)_3$ was interesting. Four methyl resonances were observed for the bidentate dithiocarbamates, and three peaks were seen for the quaternary carbons, one for each of the dithiocarbamate ligands in the molecule. By comparison with the other *cis* complexes, the peak at 205.9 ppm was assigned to the quaternary carbon of the unidentate ligand. In addition, two very broad resonances appeared at approximately 44 and 46 ppm resulting from the two methyl groups of the unidentate ligand, indicating slow rotation of the methyl groups and/or dithiocarbamate ligand. The brown product mentioned earlier gave a spectrum which was a composite of *cis*- $\text{RuNO}(\text{S}_2\text{CNMe}_2)_3$ and *trans*- $\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_2(\text{OH})$ (see Table V).

The ^1H NMR spectrum of *cis*- $[\text{RuNO}(\text{S}_2\text{CNMeEt})_2\text{X}]$ revealed a complex multiplet for the ethyl groups and four peaks of comparable intensity for the methyl groups (only three were seen for the bromo complex, one peak being more intense and unresolved). The ^{13}C NMR spectrum of the iodo complex revealed several peaks corresponding to the methyl and methylene carbons. The *N*-methyl-*N*-ethyldithiocarbamate ligand can coordinate about ruthenium to form four geometrically distinct species and thereby generate four magnetically discrete sites for each methyl or ethyl group. The ^{13}C NMR spectrum showed four distinct methyl and three methylene peaks (one of twice the intensity, indicating accidental superposition) together with two very close resonances at high field corresponding to the methyl carbons of the ethyl group. By contrast, *trans*- $\text{Ru}(\text{NO})\text{Cl}(\text{S}_2\text{CNMeEt})_2$ showed single peaks for all methyl and methylene carbons. As expected, the ^1H NMR spectrum of *cis*- $\text{Ru}(\text{NO})(\text{S}_2\text{CNEt}_2)_2\text{X}$ ($\text{X} = \text{Br}, \text{I}$) was complex due to the several multiplets arising from four inequivalent methyl and methylene groups. The ^{13}C spectrum of the iodo derivative, however, produced three distinct methylene peaks (again with one of twice the intensity) and two methyl peaks similar to the spectrum of the *N*-methyl-*N*-ethyldithiocarbamate complex.

Electronic Spectra. Each of the complexes has intense absorption bands in the ultraviolet region in the vicinity of 250–300 nm, $\epsilon > 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. A very weak absorption

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Table VI. Electronic Spectra (in CH₂Cl₂)

complex	λ , nm (ϵ , mol ⁻¹ dm ³ cm ⁻¹)
NaS ₂ CNEt ₂ ·3H ₂ O ^a	257 (1.26 × 10 ⁴), 290 (1.58 × 10 ⁴)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ Cl]	270 (3.6 × 10 ⁴), 290 (3.1 × 10 ⁴), 555 sh (~20)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ Cl]	272 (3.6 × 10 ⁴), 290 (3.3 × 10 ⁴), 550 sh (~15)
<i>trans</i> -[RuNO(S ₂ CNMePh) ₂ Cl]	270 sh (3.2 × 10 ⁴), 298 (4.3 × 10 ⁴), 550 sh (~20)
<i>trans</i> -[RuNO(S ₂ CNMeEt) ₂ Cl]	271 (3.6 × 10 ⁴), 291 (3.3 × 10 ⁴), 555 sh (~10)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ N ₃]	275 (4.0 × 10 ⁴), 555 sh (~10)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ NCO]	270 (3.7 × 10 ⁴), 555 sh (~15)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ SCN]	273 (3.7 × 10 ⁴), 350 sh (4.5 × 10 ³), 555 sh (~20)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ OH]·CH ₃ OH	278 (4.0 × 10 ⁴), 290 sh (3.1 × 10 ⁴), 555 sh (~25)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ H ₂ O]BF ₄ ^b	223 (2.6 × 10 ⁴), 276 (3.4 × 10 ⁴)
<i>trans</i> -[RuNO(S ₂ CNMe ₂) ₂ CH ₃ OH]PF ₆ ^b	223 (~3 × 10 ⁴), 277 (~3 × 10 ⁴), 550 br sh (~15)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂]	245 sh (3.3 × 10 ⁴), 266 (4.1 × 10 ⁴)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ F]	267 (~4 × 10 ⁴), 294 sh (~2 × 10 ⁴)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ Br]	268 (6.4 × 10 ⁴), 310 sh (1.4 × 10 ⁴), 550 sh (140)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ I]	258 (4.4 × 10 ⁴), 270 (4.4 × 10 ⁴), 550 br sh (230)
<i>cis</i> -[RuNO(S ₂ CNEt ₂) ₂ Br]	243 sh (2.8 × 10 ⁴), 270 (3.9 × 10 ⁴), 310 sh (1.3 × 10 ⁴), 550 sh (120)
<i>cis</i> -[RuNO(S ₂ CNEt ₂) ₂ I]	260 (3.7 × 10 ⁴), 275 (3.9 × 10 ⁴), 555 br sh (230)
<i>cis</i> -[RuNO(S ₂ CNMeEt) ₂ Br]	245 (3.0 × 10 ⁴), 269 (4.2 × 10 ⁴), 300 sh (1.5 × 10 ⁴), 540 sh (130)
<i>cis</i> -[RuNO(S ₂ CNMeEt) ₂ I]	255 sh (4.8 × 10 ⁴), 270 (5.0 × 10 ⁴), 550 sh (260)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ NO ₂] ^{1/4} ·CH ₃ OH	258 (4.0 × 10 ⁴), 555 sh (55)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ N ₃]	260 sh (3.6 × 10 ⁴), 268 (3.8 × 10 ⁴), 315 br sh (1.2 × 10 ⁴), 560 sh (100)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ SCN]	255 sh (4.8 × 10 ⁴), 270 (5.1 × 10 ⁴), 550 br sh (100)
<i>cis</i> -[RuNO(S ₂ CNMe ₂) ₂ NCO]	235 (2.6 × 10 ⁴), 265 (4.1 × 10 ⁴), 300 sh (1.7 × 10 ⁴), 560 sh (70)

^a Reference 35. ^b Recorded in methanol.

band was also seen at approximately 550 nm (Table VI). The ultraviolet absorptions most probably originate from ligand-centered transitions together with charge-transfer transitions between the ligands and metal center. A study²⁹ of dithioic acids assigned the high-energy absorptions to $\pi-\pi^*$ transitions. It was not possible to differentiate between the *cis* and the *trans* isomers on the basis of the number of bands appearing in the spectrum. On the whole, the *cis* complexes were more deeply colored. In particular the shoulders at 550 nm of the visible region were stronger for the *cis* complexes since the tail end of the ultraviolet absorptions for these compounds extended considerably into the visible region of the spectrum.

These weak visible absorption bands compare favorably with the spectra³⁰ of *cis*- and *trans*-[RuNO(X)(NH₃)₄]²⁺ (X = OAc, Cl, OH, NCO, N₃, Br) in which a weak band was observed at approximately 450 nm ($\epsilon \sim 20$ mol⁻¹ dm³ cm⁻¹). Schreiner³⁰ assigned this absorption band to a composite of ¹A₁ → [³T₁, ³T₂] and t_{2g} → π^* NO transitions.

Discussion and Conclusions

These ruthenium-dithiocarbamato-nitrosyl complexes are air-stable compounds. The *cis* isomers are brown and the *trans* species yellow to amber. In keeping with the stability of other ruthenium nitrosyl complexes, the compounds are kinetically inert. It is probably the unique stability of the [RuNO]⁶ moiety³¹ which prevented oxygen atom transfer in *cis*-RuNO(S₂CNMe₂)₂¹⁵NO₂.

The *trans* isomer is the thermodynamically favored product for almost half the complexes reported. The conversion of the kinetically formed *cis*-Ru(NO)(S₂CNMe₂)₂X (X = N₃, NCO, NCS) to the *trans* isomer upon heating is in keeping with the *cis* to *trans* isomerization commonly observed for ruthenium nitrosyl ammine complexes.³² However, many of the dithiocarbamato complexes could be isolated only with *cis* geometry: *cis*-Ru(NO)(S₂CNRR')₂X (X = Br, I; R = R' = Me or Et; R = Me, R' = Et, and X = NO₂; R = R' = Me). The

chloro ligand differed from the other halo ligands in forming the *trans* isomer exclusively.

Some comparisons with the iron-dithiocarbamato system can be drawn.¹³⁻¹⁵ In the main, the six-coordinate ruthenium complexes are more stable than their iron counterparts. For example the chloro and azido complexes of ruthenium are stable but all attempts to prepare the chloro or azido complexes of iron failed. The values of $\nu(\text{NO})$ for the ruthenium complexes are comparable with the observed values for the six-coordinate iron compounds.

Although ¹H NMR spectroscopy readily distinguishes between the *cis* and *trans* configurations of the complexes, the ¹³C NMR spectrum provided additional important information regarding the behavior of the entire dithiocarbamate ligand. This is particularly evident for *cis*-Ru(NO)(S₂CNMe₂)₂ where the ¹H NMR spectrum at room temperature exhibits a single peak for the two nonequivalent methyl groups of the monodentate dithiocarbamate ligand, while the ¹³C NMR spectrum showed a slight splitting demonstrating their nonequivalence. The temperature dependence of the NMR spectrum of Ru(NO)(S₂CNMe₂)₂ was studied in the temperature range from -40 to +150 °C. The results show that the unidentate dithiocarbamate ligand has a low barrier to rotation (~14 kcal mol⁻¹) about the C-N bond and that there is no exchange between the unidentate and the two bidentate ligands over the temperature range investigated.

Experimental Section

Ruthenium nitrosyl trichloride purchased from Engelhardt was purified by twice fuming with hydrochloric acid until a red syrup was obtained. Drying over phosphorus pentoxide, in vacuo, resulted in a red solid. Dithiocarbamate ligands were used as purchased from Aldrich and Baker. Methylenehydrazine hydrochloride was used as received from Eastman. Ammonium *N*-phenyl-*N*-methylthiocarbamate was prepared according to literature sources.^{33,34} Column chromatography was carried out on Baker neutral alumina (pH 6-8).

Microanalyses were done by MHW Laboratories, Phoenix, Ariz., and Huffman Laboratories Inc., Wheatridge, Colo. Molecular weights were determined osmotically by Huffman Laboratories, Inc. Solid infrared spectra were obtained from KBr pellets, using Perkin-Elmer

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Models 735 and 337. Melting point determinations, using a Thomas Hoover capillary melting point apparatus, were done in air and were uncorrected.

Electronic spectra were recorded by a Cary 14 spectrophotometer. Proton NMR spectra were measured in CH_2Cl_2 , CDCl_3 , or CD_3COCD_3 by using a Varian T-60 spectrometer. Broad-band-decoupled ^{13}C NMR spectra were recorded by using a Bruker WH-90. Molar conductances of 10^{-3} mol dm^{-3} solutions were determined by an Industrial Instruments conductivity bridge, Model RC-216B2.

trans-[RuNO(S₂CNRR')₂Cl]. (a) R = R' = Me. Solid $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$ (0.35 g) was added to a stirred methanolic solution (15 cm³) of $\text{RuNOCl}_3 \cdot \text{XH}_2\text{O}$ (0.25 g). The initial red-violet solution quickly changed to brown with gradual deposition of a tan precipitate. After 30 min, the solid was collected and washed with a mixture of $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ leaving a yellow solid; yield 0.075 g, 20%. When the reaction was carried out by heating the reagents in methanol, followed by adding dilute HCl (~5 cm³) and boiling, a higher yield of the complex was obtained (0.2 g, 50%). The complex was recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ yielding yellow-orange needles.

(b) R = R' = Et. Solid $\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$ (0.32 g) was added to a stirred methanolic solution of $\text{RuCl}_3\text{NO} \cdot \text{XH}_2\text{O}$ (0.18 g). After a deep brown coloration developed, concentrated HCl (1 cm³) was added and the solution boiled. A yellow product was collected and washed with methanol (0.12 g, 36%). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ gave yellow crystals.

(c) R = Me, R' = Et. Addition of $\text{NaS}_2\text{CNMeEt} \cdot 2\text{H}_2\text{O}$ (0.41 g) to $\text{RuCl}_3\text{NO} \cdot \text{XH}_2\text{O}$ (0.25 g) in methanol gave a brown solution which yielded a yellow product upon addition of HCl and boiling (0.19 g, 45%). The complex was washed with water and methanol. Purification was achieved by passage of a CH_2Cl_2 solution of the complex through neutral alumina or by recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$.

(d) R = Me, R' = Ph. Addition of freshly prepared $\text{NH}_4\text{S}_2\text{CNMePh}$ (0.32 g) to a stirred methanolic solution of $\text{RuNOCl}_3 \cdot \text{XH}_2\text{O}$ (0.2 g) yielded a tan product. Washing with water, methanol, and ether left a yellow solid (0.06 g, 15%). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ gave yellow crystals.

cis-[RuNO(S₂CNMe₂)₃]/trans-[RuNO(S₂CNMe₂)₂OH]. (a) This mixture was isolated from the preparation of *trans*-[RuNO-(S₂CNMe₂)₂Cl] provided the mother liquor was not acidified. After collection of the yellow complex, the brown filtrate deposited brown microcrystals on standing overnight (0.06 g, 16%).

(b) Refluxing 3 equiv of $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$ (0.53 g) with $\text{RuCl}_3\text{NO} \cdot \text{XH}_2\text{O}$ (0.25 g) in methanol gave a brown solution and some insoluble *trans*-chloro complex. After filtration and refluxing for about 10 min, brown microcrystals were obtained on standing (0.18 g, 50%). Microanalysis and IR and NMR spectra of this brown material revealed that it contains bidentate and unidentate dithiocarbamate ligands (3:1) and a coordinated hydroxyl group. A molecular weight determination indicated the presence of monomeric species. The solutions were nonconducting (Table I). Chromatography of this brown mixture resulted in isolation of $\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_3$ and *trans*- $\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_2(\text{OH})$ in a ratio of 2:1. Comparison with a genuine sample of $\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_3$ indicates that it was present in the original mixture. The properties of the hydroxo complex isolated from the mixture were identical with those of an independently prepared sample.

cis-[RuNO(S₂CNMe₂)₃]. Refluxing 0.1 g of brown product with a large excess of $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$ (~0.2 g) in methanol yielded a red-brown solution. When the mixture was allowed to stand, deep red crystals appeared (0.05 g, 48%). These were collected and washed with methanol. Recrystallization was possible from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$.

cis-[RuNO(S₂CNRR')₂Br]. (a) R = R' = Me. A suspension of *trans*-[RuNO(S₂CNMe₂)₂Cl] (0.1 g) in methanol was refluxed with excess HBr (48% soln) until a brown solution was obtained. Evaporation gave brown microcrystals. Column chromatographic purification showed a single brown band. Recrystallization was accomplished from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$; yield 0.095 g, 85%. The complex was also isolated on boiling *cis*-[RuNO(S₂CNMe₂)₃] (yield 63%) or the brown product (yield 45%) with HBr in methanol.

(b) R = R' = Et. A methanolic solution of *trans*-[RuNO-(S₂CNEt₂)₂Cl] (0.05 g) was refluxed with excess HBr (48%) for 30 min. The brown solution was evaporated and the solid washed with water and ether. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ gave light brown crystals (0.03 g, 55%).

(c) R = Me, R' = Et. A methanolic solution of *trans*-[RuNO-(S₂CNMeEt)₂Cl] (0.1 g) and excess HBr (48% soln) was refluxed

for approximately 40–50 min. The brown solution gave a brown solid (0.09 g, 82%), which was washed with water and ether. It was purified by dissolving in a minimum volume of CH_2Cl_2 followed by passage through a neutral alumina column (12 in. $\times$ 1/2 in.). A single brown band was eluted with CH_2Cl_2 . Addition of CH_3OH to the brown effluent yielded brown crystals on standing.

cis-[RuNO(S₂CNRR')₂I]. (a) R = R' = Me. Refluxing a suspension of *trans*-[RuNO(S₂CNMe₂)₂Cl] (0.16 g) with excess HI (48%) for several hours gave a dark brown mixture. A dark brown product was collected, washed with methanol, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$; yield 0.17 g (90%). Boiling *cis*-[RuNO(S₂CNMe₂)₃] or the brown product with HI in methanol also yielded the same product (yield ~80%).

(b) R = R' = Et. The *trans*-[RuNO(S₂CNEt₂)₂Cl] complex (0.05 g) was refluxed with excess HI (48%) for 30 min. Overnight evaporation gave brown crystals. Recrystallization was from $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$; yield 0.04 g (68%).

(c) R = Me, R' = Et. A methanolic solution of *trans*-[RuNO-(S₂CNMeEt)₂Cl] (0.1 g) and excess HI (48% soln) was refluxed for 45 min. A dark brown solid was isolated and washed with water (0.1 g, 84%). Purification was achieved by dissolving the product in a minimum amount of CH_2Cl_2 followed by passage through a neutral alumina column (12 in. $\times$ 1/2 in.). A single brown band was eluted. Addition of CH_3OH to the brown effluent gave brown crystals on standing.

cis-[RuNO(S₂CNMe₂)₂F]. A sample of *cis*-[RuNO(S₂CNMe₂)₃] (0.07 g) was suspended in methanol in a plastic beaker. Excess HF (48% soln) was added and the mixture heated until the solid dissolved giving a brown solution. On cooling of the solution, a brown solid formed which was collected and washed with ether; yield 0.04 g, 72%. The product was extracted into CH_2Cl_2 to which CH_3OH was added. A brown microcrystalline solid was isolated. Treatment of the brown product in like manner gave the same solid.

cis-[RuNO(S₂CNMe₂)₂NO₂]^{1/4}·CH₃OH. A suspension of *cis*-[RuNO(S₂CNMe₂)₂I] (0.01 g) and AgNO_2 (0.04 g) in methanol was refluxed for approximately 5–10 min. A color change from dark brown to tan occurred. Cooling and filtering yielded a golden brown solution which gave a light brown solid on evaporation (0.067 g, 80%). The product was redissolved in a minimum of CH_2Cl_2 and passed through an alumina column. A brown band was readily eluted with CH_2Cl_2 , leaving a thin brown band unshifted at the top of the column. Methanol was added to the eluted fraction which gave brown crystals upon evaporation; yield 60%. The product was washed with ether. The unshifted band was readily eluted with methanol and identified as *trans*-[RuNO(S₂CNMe₂)₂OH]·CH₃OH (yield ~9%).

The labeled complex *cis*-[RuNO(S₂CNMe₂)₂¹⁵NO₂] was prepared from $\text{Ag}^{15}\text{NO}_2$ (¹⁵N 99%). In CDCl_3 the labeled complex revealed a ¹⁵N resonance 87.8 ppm downfield from $\text{Na}^{15}\text{NO}_3$.

trans-[RuNO(S₂CNMe₂)₂H₂O]BF₄. To a methanolic suspension of the nitro complex (0.065 g) in a plastic beaker was added excess HBF_4 (48% soln) and the mixture heated until the complex dissolved, giving a yellow solution. On cooling of the solution, tiny yellow needles appeared. These were collected and washed with ether; yield 0.05 g, 70%.

trans-[RuNO(S₂CNMe₂)₂CH₃OH]PF₆. A suspension of the iodo complex (0.06 g) and AgPF_6 (0.06 g) in dissolved, dried methanol was heated for several minutes. A yellow suspension developed rapidly. Upon cooling and filtering of the solution, a yellow solution was obtained which yielded a yellow product upon evaporation. This was washed with ether; yield 0.06 g, 90%. Recrystallization from methanol gave yellow crystals. Refluxing *trans*-[RuNO(S₂CNMe₂)₂Cl] with AgPF_6 in dried methanol for about 30–60 min gave the same product; yield 72%.

trans-[RuNO(S₂CNMe₂)₂OH]·CH₃OH. A brown suspension of the iodo complex (0.1 g) and Ag_2O (0.07 g) was refluxed together in methanol for 15 min. The yellow-brown mixture was cooled and filtered, yielding a golden brown filtrate from which amber crystals were isolated; yield 0.065 g, 76%. Recrystallization was from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$.

[RuNO(S₂CNMe₂)₂N₃]. (a) Cis Isomer. A suspension of *cis*-[RuNO(S₂CNMe₂)₂I] (0.1 g) and AgN_3 (0.04 g) was refluxed in methanol for about 5 min. A tan coloration developed. After cooling and filtering of the solution, a light brown solid was obtained from the filtrate; yield 0.07 g, 85%. Dissolution in CH_2Cl_2 and passage through a neutral alumina column gave a brown band, readily elutable with CH_2Cl_2 . Methanol was added to the effluent and brown crystals

were obtained on standing.

(b) Trans Isomer. (i) Refluxing *trans*-[RuNO(S₂CNMe₂)₂Cl] (0.09 g) and AgN₃ (0.08 g) in methanol for ~6 h gave a brown suspension. Filtration, followed by evaporation, gave a brown solid (0.05 g). This was dissolved in a minimum amount of CH₂Cl₂ and passed through neutral alumina (12 in. × 1/2 in.). The *trans* isomer was eluted with CH₂Cl₂ as a yellow band. Methanol was added, and orange needles were obtained on standing; yield 0.022 g (24%). A thin brown band of the hydroxo complex remained at the head of the column. When *trans*-[RuNO(S₂CNMe₂)₂Cl] was refluxed with AgN₃ for only 2 h, lower yields of the *trans* isomer were obtained (4%). The *cis* isomer was eluted second from the column (20%).

(ii) A more convenient preparation entailed heating solid *cis*-[RuNO(S₂CNMe₂)₂N₃] in air to a temperature of approximately 180 °C. At ca. 150 °C, the brown crystals changed to yellow. The sample was left at 170–180 °C for approximately 10 min. The yellow product was washed with diethyl ether.

[RuNO(S₂CNMe₂)₂SCN]. (a) Cis Isomer. The method described for the azido complex was followed. The yield of product from 0.06 g of *cis*-[RuNO(S₂CNMe₂)₂I] and 0.025 g of AgSCN was 0.045 g, 85%. Dissolution in CH₂Cl₂ and passage through an alumina column showed only traces of *trans* isomer (pale yellow band) which eluted first. The *cis* isomer was present as a brown band. Recrystallization from CH₂Cl₂/CH₃OH gave brown crystals.

(b) Trans Isomer. Solid *cis*-[RuNO(S₂CNMe₂)₂SCN] was heated in air to approximately 220 °C. At 210–215 °C, a color change from brown to tan occurred. Under the microscope the product appeared as tiny yellow crystals. The sample was left at 220 °C for about 10 min. The product was then washed with ether and recrystallized from CH₂Cl₂/CH₃OH.

Poor yields of the complex were obtained by refluxing *trans*-[RuNO(S₂CNMe₂)₂Cl] (0.1 g) with AgSCN (0.09 g) in methanol for 4 h. The brown product (0.09 g) obtained after filtration was treated as for the *cis* isomer. The *trans* isomer was eluted first (4%) followed by the *cis* complex (15%). The *trans* hydroxo complex remained at the head of the column.

[RuNO(S₂CNMe₂)₂NCO]. (a) Cis Isomer. (i) A mixture of *cis*-[RuNO(S₂CNMe₂)₂I] (0.1 g) and AgNCO (0.05 g) was refluxed in methanol for 10 min. A color change from brown to yellow occurred. A yellow-brown solid was isolated after filtration. Dissolution in CH₂Cl₂ and passage through neutral alumina gave a light brown band which was readily eluted with CH₂Cl₂. Khaki crystals were obtained; yield 0.015 g, 18%. A second yellow band, not shifted by CH₂Cl₂, was readily eluted with CH₃OH and yielded amber crystals

of *trans*-[RuNO(S₂CNMe₂)₂OH]·CH₃OH; yield 0.015 g, 18%.

(ii) Heating *cis*-[RuNO(S₂CNMe₂)₂] (0.1 g) in acetonitrile with a slight excess of AgPF₆, followed by cooling and filtering, gave a yellow-orange solution. Solid KNCO (0.05 g) was added and a brown solution resulted after boiling the mixture for several minutes. The solid was treated as in (i). The yellow *trans* isomer was eluted first (5%) followed by the *cis* isomer (25%).

(b) Trans Isomer. Heating solid *cis*-[RuNO(S₂CNMe₂)₂NCO] in air to approximately 175 °C resulted in quantitative conversion to the yellow *trans* isomers. The product was washed with ether.

Sodium *N*-Methyl-*N*-ethylidithiocarbamate. *N*-Methyl-*N*-ethylamine hydrochloride (1 g) was dissolved in chilled methanol (10 cm³). Addition of CS₂ (1 cm³) was followed by an aqueous solution of NaOH (1 g in a minimum volume). Stirring gradually gave a yellow solution which upon slow evaporation yielded white crystals. These were collected, washed with ether and pentane, and recrystallized twice from methanol. The mother liquor yielded several batches of crystals: total yield 1.4 g, 64%; mp 113–115 °C.

Silver Salts. These were prepared by metathesis from silver nitrate and the required sodium salt. The labeled nitrite, Ag¹⁵NO₂, was prepared from AgClO₄ and Na¹⁵NO₂ (¹⁵N 99%); yield 76%.

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Registry No. *trans*-[RuNO(S₂CNMe₂)₂Cl], 72075-88-8; *trans*-[RuNO(S₂CNEt₂)₂Cl], 72075-89-9; *trans*-[RuNO(S₂CNMePh)₂Cl], 72075-90-2; *trans*-[RuNO(S₂CNMeEt)₂Cl], 72075-91-3; *trans*-[RuNO(S₂CNMe₂)₂N₃], 72075-92-4; *trans*-[RuNO(S₂CNMe₂)₂NCO], 72075-93-5; *trans*-[RuNO(S₂CNMe₂)₂SCN], 72075-94-6; *trans*-[RuNO(S₂CNMe₂)₂OH], 72075-95-7; *trans*-[RuNO(S₂CNMe₂)₂H₂O]BF₄, 72075-97-9; *trans*-[RuNO(S₂CNMe₂)₂CH₃OH]PF₆, 72075-99-1; *cis*-[RuNO(S₂CNMe₂)₂], 51139-59-4; *cis*-[RuNO(S₂CNMe₂)₂F], 72076-00-7; *cis*-[RuNO(S₂CNMe₂)₂Br], 72076-01-8; *cis*-[RuNO(S₂CNMe₂)₂I], 72076-02-9; *cis*-[RuNO(S₂CNEt₂)₂Br], 72076-03-0; *cis*-[RuNO(S₂CNEt₂)₂I], 72076-04-1; *cis*-[RuNO(S₂CNMeEt)₂Br], 72076-05-2; *cis*-[RuNO(S₂CNMeEt)₂I], 72076-06-3; *cis*-[RuNO(S₂CNMe₂)₂NO₂], 72076-07-4; *cis*-[RuNO(S₂CNMe₂)₂N₃], 72120-76-4; *cis*-[RuNO(S₂CNMe₂)₂SCN], 72120-77-5; *cis*-[RuNO(S₂CNMe₂)₂NCO], 72120-78-6; RuNOCl₃, 18902-42-6.

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Novel Transition-Metal Complexes of Camphorquinone Dioxime Ligands

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Camphorquinone dioxime, H₂CQD, is known to exist in four isomeric forms (α , β , γ , and δ) which differ by the orientations of the OH groups on their oxime nitrogen atoms. The deprotonated β -HCQD⁻ coordinates via the two N atoms to form the square-planar complexes Pd(β -HCQD)₂, Pt(β -HCQD)₂, and Cu(β -HCQD)₂·H₂O.^{1/2}dioxane. However, δ - and α -HCQD⁻ coordinate via one N and one O atom to yield square-planar complexes of the type Pd(δ -HCQD)₂, Ni(δ -HCQD)₂, and Ni(α -HCQD)₂. The neutral β -H₂CQD ligand forms Pd(β -H₂CQD)Cl₂, Pt(β -H₂CQD)Cl₂, and Cu(β -H₂CQD)Cl₂ complexes in which the ligand coordinates through both N atoms. Spectroscopic evidence indicates that α -, γ -, and δ -H₂CQD are monodentate ligands, coordinating via only one N atom, in Pd(α -H₂CQD)₂Cl₂, Pd(γ -H₂CQD)₂Cl₂, and Pd(δ -H₂CQD)₂Cl₂. Finally, structures for two complexes of the unusual composition Ni(δ -HCQD)₂(δ -H₂CQD)₂ and [Pt(γ -HCQD)(γ -H₂CQD)Cl]₂ have been suggested. Ultraviolet-visible, infrared, ESR, and ¹H NMR spectroscopy were employed to characterize these new types of α -dioxime complexes.

Introduction

The chemistry of transition-metal complexes with α -dioxime ligands has been well studied and is the subject of several reviews.¹⁻⁵ Yet little was known about the coordination

chemistry of transition metals with the camphorquinone dioxime ligands, H₂CQD, until last year when work in this laboratory⁶ and in Osaka University⁷⁻⁹ was reported.

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