COMMUNICATION

CONVENIENT, STRAIGHTFORWARD ROUTES TO CARBODITHIOATO DERIVATIVES OF WEAK NITROGENOUS NUCLEOPHILES

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Abstract—The N-alkyldithiocarbamate ligands when bidentately-coordinated to the nickel triad elements undergo facile electrophilic substitution reactions with a diversity of electrophiles affording novel carbodithioato derivatives of weak nitrogenous bases, not available by other methods.

In the course of our investigations on the reactions of the square-planar d^8 bis(N-alkyldithiocarbamato)metal(II) complexes with Lewis bases (L), we have demonstrated that dithiocarbimato complexes formulated as $[M(S_2C=NR)L_2]$ and $[M(S_2C=NR)_2]^{2-}$ can be isolated.¹⁻⁴ The mechanism of these reactions at the level of the frontier molecular orbital approach of chemical reactivity has been fully investigated by EHMO-SCCC calculations.⁵ According to these investigations, the acidic character of the hydrogen atom of the bidentately-coordinated parent N-alkyldithiocarbamate ligands, as well as the high nucleophilicity of the nitrogen atom of the resulted dithiocarbimate ligands, have been verified. It is readily apparent from these reactivity patterns that the square-planar d^8 [M(S₂CNHR)₂] complexes could easily undergo electrophilic substitution reactions, affording new classes of carbodithioato complexes, according to Scheme 1.

Taking advantage of this reactivity pattern, convenient, straightforward routes to carbodithioato derivatives of weak nitrogenous bases, such as secondary amides, ureas, amino acid esters, carbamic

esters and sulphonamides, have emerged. In this respect, some of the resulting novel carbodithioate ligands are shown in Table 1. The direct preparation of such ligands by the reaction of the corresponding weak nitrogenous base with carbon disulphide in alkaline media is difficult or impossible to achieve, although some examples concerning the formation of N-formyl and N-methyl N-formyl dithiocarbamates and their thioformyl analogues have already been published.⁶⁻¹⁰ However, no reports on their corresponding coordination compounds with transition metals have been found by us to date. Therefore, the novel nickel(II) complexes of the aforesaid carbodithioate ligands reported herein are probably some of the first examples in the pure chemistry of the dithiocarbamate ligands which may be considered as derivatives of weak nitrogenous bases. It is important to note, at this point, that all our efforts to prepare the corresponding free ligands according to the procedure described by Gattow et al.⁶ were unsuccessful, leading to unstable easily oxidized species.

In a typical reaction concerning the synthesis of the bis(N-alkyl N-acetyldithiocarbamato)nickel(II)



Table 1. Representative electrophilic substitution reactions of square-planar bis(N-alkyldithiocarbamato)nickel(II) complexes

Electrophile	Precursor	Carbodithioato ligand ^{a,b}		
[MeCO] ⁺	(MeCO) ₂ O	[R(MeCO)NCS ₂] ⁻		
[PhCO] ⁺	PhCOC1	[R(PhCO)NCS ₂] ⁻		
PhN=C=O	PhN=C=O	[R(PhHNCO)NCS ₂] ⁻		
[Ph ₂ NCO] ⁺	Ph ₂ NCOCl	$[R(Ph_2NCO)NCS_2]^-$		
[MeOCOCH ₂] ⁺	ClCH ₂ COOMe	$[R(CH_2COOMe)NCS_2]^-$		
[EtOCO] ⁺	ClCOOEt	$[R(COOEt)NCS_2]^-$		
[ArSO ₂] ⁺	ArSO ₂ Cl	$[R(ArSO_2)NCS_2]^-$		

^{*a*} Depending on the reaction conditions, one or both the dithiocarbamato ligands could undergo an electrophilic substitution reaction.

^b $\mathbf{R} = alkyl \text{ or } aryl; Ar = Ph, p-MePh.$

complexes,¹¹ [Ni{S₂CN(COMe)R}₂] (R = Me, Et, Bu', Bz, Ph, p-MePh, p-ClPh), the following procedure was adopted: 1 mmol of the appropriate [Ni(S₂CNHR)₂] complex was dissolved in acetone and treated with 2 mmol of triethylamine and 2 mmol of acetic anhydride. In the resulting solution a solid material was formed, which on addition of water was quantitatively separated. Purification was achieved by dissolving the solid in chloroform and re-precipitating with ethanol (yield: 75%). It should be noted that by changing the molar ratio of the reactants to 1:1:1, the mixed-ligand (Nalkyldithiocarbamato)(N-alkyl N-acetyldithiocarbamato)nickel(II) complexes can also be isolated in relatively high yields. A similar procedure was followed for the synthesis of the rest of the carbodithioato nickel(II) complexes by using the appropriate precursor of the corresponding electrophile. Obviously, in the case of $[Ni{S_2CN} (PhHNCO)R}_2]$ complexes, the presence of triethylamine as the deprotonating agent was unnecessary. All of these compounds are non-conducting, diamagnetic, and quite stable both in solid and solution states.

Inspection of the spectroscopic (Table 2) and magnetic data of the compounds under study clearly indicates the bidentate bonding mode of the carbodithioate ligands in the complexes and their

Table 2. Spectral data of some representative nickel(II) carbodithioates

	IR ⁴			UV–vis ^b	
Compound	v(CO)	v(CN)	v(CSS)	v(NiS)	v/kK
$[Ni{S_2CN(MeCO)Me}_2]$	1713vs	1453m	994vs	397m	30.6, 26.7sh, 21.5, 18.8sh, 16.2sh
$[Ni{S_2CN(PhCO)Me}_2]$	1724vs	1590m	980m	390m	30.2, 26.0sh, 21.3, 18.5sh, 15.6sh
[Ni{S ₂ CN(PhHNCO)Me} ₂]	1687vs	1537s	965m	385m	30.8, 26.8sh, 23.8, 21.1, 15.8sh
[Ni{S ₂ CN(Ph ₂ NCO)Me} ₂]	1720vs	1550s	1003m	380w	30.9, 26.3sh, 24.1, 20.7, 15.7sh
[Ni{S ₂ CN(CH ₂ COOMe)Me}]]	1750vs	1526vs	1012m	387m	31.1, 25.8sh, 23.5, 20.9, 15.8sh
[Ni{S ₂ CN(COOEt)Me} ₂]	1731vs	1433m	982w	393w	31.0, 26.7sh, 21.8, 20.2sh, 18.9sh
$[Ni{S_2CN(PhSO_2)Me}_2]^c$		1447m	998w	392w	30.5, 26.0sh, 22.3, 19.5sh, 16.3sh

^a KBr discs.

^bCHCl₃ solutions.

 $v_{as}(SO_2)$, 1367vs cm⁻¹; $v_s(SO_2)$, 1169vs cm⁻¹.

square-planar configuration. Although all the ligands also possess an oxygen donor atom capable of bonding to the central atom forming a six-membered chelate ring, involving O- and S-coordination, such bonding has been excluded on the basis of spectroscopic data. Therefore, all these new compounds have broadly similar structures, involving the square-planar NiS₄ chromophore. However, in order to establish further their geometries, an X-ray diffraction study has been carried out on a member of this series, namely the [Ni{S₂CN (COMe)Bz}₂] complex.¹²

Obviously, any attempt to further extend these electrophilic substitution reactions by using a great diversity of electrophiles, as well as other transition metal ions, would be of great importance, for it is possible to obtain novel compounds whose structures, chemical reactivities and applications are worth studying. Some of them, especially those of iron(III), are expected to extend further the area of six-coordinated iron complexes exhibiting either the low-spin configuration or intermediate spin states. Moreover, it is possible to obtain indirectly, via degradation of the complexes, organic and biorganic compounds involving peptide-type bonds. Work along these lines is continuing in our laboratory.

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