

AMMINES OF CHROMIUM(II) ACETATE

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Abstract

The water molecules in $[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{OH}_2)]_2$ are replaced by ammonia when the gas is bubbled through a suspension of the hydrate in ethanol, but the binuclear structure is destroyed in liquid ammonia from which $\text{Cr}(\text{NH}_3)_4(\text{O}_2\text{CCH}_3)_2$ has been isolated.

Results and Discussion

The isostructural, binuclear nature of chromium(II) and copper(II) acetates $[\text{M}(\text{O}_2\text{CCH}_3)_2(\text{OH}_2)]_2$ has long been known (1) and more recently it has been shown (2) that the Cr-Cr distance is 2.362 Å rather than 2.64 Å as earlier reported. The shorter distance is much more compatible with the strong antiferromagnetic interaction (3) found in anhydrous and hydrated chromium(II) acetate, and the quadruple bond description of the Cr-Cr interaction (4). Various amines such as pyridine (5,6), substituted pyridines (7), piperidine (7,8) and pyridine (6) can replace the water molecules in chromium(II) acetate without disrupting the binuclear structure, pyrazine forming a 1:1 adduct in which the difunctional amine bridges $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ units, but there seems to be no report of attempts to substitute water by ammonia in copper(II) acetate, and only a brief statement (5) that an ammonia adduct can be obtained by passing ammonia through chromium(II) acetate suspended in benzene.

The copper(II) complex $\text{Cu}(\text{NH}_3)_2(\text{O}_2\text{CCH}_3)_2$ can be obtained (9) by dissolving the binuclear acetate in concentrated aqueous ammonia, and we have found that the reaction of ammonia gas with the acetate suspended in ethanol gives the same compound rather than a mono-ammine, i.e. the Cu-Cu bond is easily broken. However, it is more difficult to disrupt the Cr-Cr bond as the reddish-purple mono-ammine $\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)$ has been prepared by passing dry ammonia through a suspension of chromium(II) acetate monohydrate in ethanol.

Like the monohydrate, the mono-ammine is very weakly paramagnetic, with an effective magnetic moment of 0.6 B.M. at 295K which decreased to approximately 0.3 B.M. at 90K (Table 1). However, the calculation of the magnetic moment incorporates the temperature, and with such low moments the molar susceptibility χ_{Cr} is more significant. As χ_{Cr} is essentially independent of temperature, it can be assumed to arise from temperature independent paramagnetism. Chromium(III) impurities would cause χ_{Cr} to

TABLE 1
Magnetic Behaviour

Compound	T(°K)	$10^6 \chi_{\text{Cr}}$ (c.g.s.)	μ_{eff} (B.M.) ^a
$[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)]_2$	295.0	133	0.56
	263.5	125	0.51
	245.0	120	0.48
	230.4	131	0.49
	198.2	121	0.44
	166.2	127	0.41
	145.5	117	0.37
	135.2	127	0.37
	103.7	115	0.30
	89.4	95	0.26
(diamagnetic correction = -78×10^{-6} c.g.s.)			
$\text{Cr}(\text{NH}_3)_4(\text{O}_2\text{CCH}_3)_2$	295.0	9497	4.73
(diamagnetic correction = -132×10^{-6} c.g.s., $\theta^a = 1^\circ$)			

^aCalculated from $\mu_{\text{eff}} = 2.828 \sqrt{\chi_A T}$ B.M. and $\chi_{\text{Cr}}^{-1} \propto (T + \theta)$.

increase at the lowest temperatures (3), but this did not happen with the mono-ammine. The magnetic data show that unlike in copper(II) acetate monohydrate there is insignificant population of the triplet state at room temperature so that the singlet-triplet separation must be large ($2J > 1000 \text{ cm}^{-1}$), but magnetic data are too insensitive to changes in J when J is large for meaningful estimates to be made.

The X-ray powder patterns of $[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{OH}_2)]_2$ and $[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)]_2$ are similar although the complexes are not isomorphous. Except where NH vibrations occur, the i.r. spectrum is like the spectra (10) of hydrated copper(II) and chromium(II) acetates. The N-H stretching vibrations occur at 3330 and 3290 cm^{-1} , but the asymmetric NH_3 deformation expected at ca. 1600 cm^{-1} is obscured by the intense asymmetric carboxylate stretching absorption at 1580 cm^{-1} . The symmetric ammine deformation occurs at 1180 cm^{-1} , but the rocking vibration expected near 680 cm^{-1} cannot be distinguished from acetate absorptions. A band at 475 cm^{-1} can be assigned to the Cr-N stretching vibration as no absorption is present at this frequency in the spectrum of the hydrate.

Reaction of liquid ammonia with $[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)]_2$ breaks the Cr-Cr bond because it produced the violet tetra-ammine $\text{Cr}(\text{NH}_3)_4(\text{O}_2\text{CCH}_3)_2$ which obeys the Curie law (Weiss constant $\theta \approx 0^\circ$), with an effective magnetic moment close to the spin-only value (4.9 B.M.) for the high-spin $3d^4$ configuration (Table 1).

The tetra-ammine is thus a magnetically-dilute chromium(II) compound, and is presumably mononuclear. The broad asymmetric band at 17200 cm^{-1} in its reflectance spectrum (Table 2) is similar to that found (11) in the spectrum of $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)]\text{SO}_4$. The sulphate is isomorphous with the corresponding

TABLE 2
Diffuse Reflectance Spectra

Compound	$\bar{\nu}(\text{cm}^{-1})$			
$[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)]_2$	RT ^a	37000s,b	$\sim 29000\text{s}, \text{vb}^b$	19500s,b
	LT	37000s,b	$\sim 29000\text{s}, \text{vb}^b$	20000s,b
$\text{Cr}(\text{NH}_3)_4(\text{O}_2\text{CCH}_3)_2$	RT	38000s,b	30000w 28200sh	17200s,b
	LT	38000s,b	30000w 27800w	17700s 13500sh

^aReflectance bands at room (RT) and liquid nitrogen (LT) temperatures.

^bThis very broad band appears to be a composite of absorptions at 29800, 28600 and 27700 cm^{-1} .

copper(II) compound which is known (12) to have a structure in which oxygen atoms from water molecules are 2.59 and 3.37 Å from planar $[\text{Cu}(\text{NH}_3)_4]^{2+}$ units. The tetra-ammine may have a similar structure in which trans-monodentate acetate ions are different distances from the chromium ions, but other structures are possible. The breadth of the reflectance band is compatible with a highly distorted structure leading to overlapping of the transitions $^5\text{B}_1 \rightarrow ^5\text{A}_1$, $^5\text{B}_1 \rightarrow ^5\text{B}_2$, and $^5\text{B}_1 \rightarrow ^5\text{E}$. Unfortunately, the tetra-ammine acetate loses ammonia and reverts to the mono-ammine so readily that i.r. spectra, which might have given information on the nature of the acetate groups, could not be obtained.

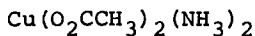
The diffuse reflectance spectra of the mono-ammine $[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)]_2$ (Table 2) and the double sulphate $\text{Cs}_2\text{SO}_4 \cdot \text{CrSO}_4 \cdot 2\text{H}_2\text{O}$, which is believed (13) to contain the sulphate-bridged anion $[\text{Cr}_2(\text{SO}_4)_4(\text{OH}_2)_2]^{4-}$, and the spectrum of $[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{OH}_2)]_2$ in ethanol (14), each have a broad and moderately intense band in the range 18000 to 21000 cm^{-1} . Comparison with the spectrum of the tetra-ammine shows that this band is at too high a frequency to be due to the d-d absorptions of a predominantly CrO_4 chromophore although it may obscure them. It is suggested that these bands correspond to the lowest energy transition ($\delta \rightarrow \delta^*$) of the binuclear system.

In many reactions of chromium(II) acetate in non-aqueous solvents the integrity of the Cr_2^{4+} unit is maintained; consequently, many quadruply bonded derivatives have been isolated (4). The knowledge that the unit can be dis-

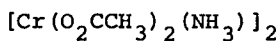
rupted in liquid ammonia may prove useful in the synthesis of mononuclear chromium(II) complexes.

Experimental

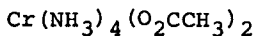
The chromium(II) complexes were prepared and handled under nitrogen, ammonia, or in vacuo.



When anhydrous ammonia gas was bubbled through a suspension of copper(II) acetate monohydrate (2.0g) in absolute ethanol (20 cm³) the turquoise solid dissolved to give a blue solution. The solution was concentrated to half volume, and cooled to 0°C. The blue crystals of $\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)_2$ which separated after some hours were filtered off, washed with ethanol and ether, and dried. Calc. for $\text{C}_4\text{H}_{12}\text{CuN}_2\text{O}_4$: C, 22.3; H, 5.6; N, 13.0%. Found: C, 22.2; H, 5.7; N, 13.3%.



The red-purple chromium(II) acetate mono-ammine separated in good yield when ammonia gas was bubbled through a suspension of chromium(II) acetate monohydrate (1.9g) in ethanol (35 cm³). It was washed with ethanol, dried in vacuum, and preserved in sealed tubes. It slowly turns brown in the air. Calc. for $\text{C}_4\text{H}_9\text{CrNO}_4$: C, 25.7; H, 4.8; N, 7.5; Cr, 27.8%. Found: C, 25.5; H, 5.0; N, 7.4; Cr, 27.3%.



This was prepared by condensing liquid ammonia on to $[\text{Cr}(\text{O}_2\text{CCH}_3)_2(\text{NH}_3)]_2$. As soon as the violet compound had formed the excess of ammonia was allowed to evaporate, and the compound was dried with a stream of ammonia. It was preserved in sealed tubes in an atmosphere of ammonia, and microanalyses could not be obtained because it lost ammonia so readily. The metal analysis was satisfactory. Calc. for $\text{C}_4\text{H}_{18}\text{CrN}_4\text{O}_4$: Cr, 21.8%. Found: Cr, 21.75%.

Magnetic measurements were carried out by the Gouy method on apparatus obtained from Newport Instruments, Newport Pagnell, Bucks. Electronic spectra were recorded on a Unicam SP 700C spectrophotometer with the SP 735 diffuse reflectance accessory. A lithium fluoride reference was used. For magnetic and spectroscopic measurements the mono-ammine was sealed in the susceptibility tube or reflectance cell in vacuo but the tetra-ammine was sealed in an ammonia atmosphere. Infrared spectra were recorded on a Perkin Elmer 577 spectrophotometer. The nujol mulls (between KBr discs) were prepared in a glove bag under nitrogen.

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