

Metal Complexes of the 2-Hydroxy Derivative of Pyridine N-Oxide

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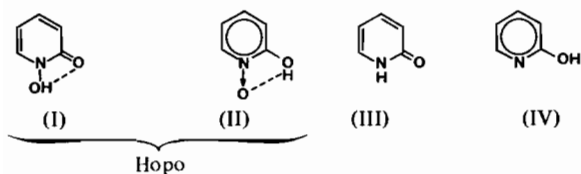
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The 2-hydroxy derivative of pyridine N-oxide exists in the tautomeric form 1-hydroxy-2-pyridone (Hopo). This paper describes the following complexes of the deprotonated ligand (opo): $\text{Cu}(\text{opo})_2$; $\text{Cu}(\text{opo})\text{NO}_3 \cdot \text{H}_2\text{O}^*$; $\text{Cu}(\text{opo})\text{Br} \cdot 0.5\text{CH}_3\text{OH}^*$; $\text{Cu}(\text{opo})\text{Cl}^*$; $\text{Ni}(\text{opo})\text{Cl} \cdot 1.5\text{H}_2\text{O}^*$; $\text{Co}(\text{opo})\text{Cl} \cdot 1.5\text{H}_2\text{O}^*$ and $\text{Fe}(\text{opo})_3 \cdot \text{H}_2\text{O}$ (new complexes are marked with asterisks). Structures with bidentate opo, are proposed for the complexes, on the basis of measurements of X-ray powder diffraction spectra, Mössbauer, infrared and electronic spectra, and magnetic data down to 89 K. The complex $\text{Cu}(\text{opo})\text{Br} \cdot 0.5\text{CH}_3\text{OH}$ is antiferromagnetic, and its susceptibility data have been fitted to various models.

Introduction

The coordination chemistry of pyridine N-oxide and its substituted forms has been thoroughly investigated [1, 2]. In spite of this there has been only limited study [2] of complexes of pyridine N-oxides with donor substituents in the 2-position. This paper deals with the 2-hydroxy derivative of pyridine N-oxide (Hopo).

The ligand Hopo is thought to exist mainly as the tautomer 1-hydroxy-2-pyridone, (I), rather than as 2-hydroxypyridine N-oxide, (II), on the basis of



spectroscopic measurements [3–7]. No X-ray structure analyses have been reported on Hopo or on its complexes.

The parent pyridine of Hopo is known to exist mainly as the tautomer 2-pyridone (III) rather than as 2-hydroxypyridine (IV), on the basis of X-ray

structure work [8, 9]. The structure of the complex $[\text{Cu}(\text{2-pyridone})_6](\text{ClO}_4)_2$ shows that the pyridone structure is maintained when 2-pyridone coordinates [10].

The ligand Hopo coordinates in the deprotonated form opo, and the following complexes have been reported previously [4, 11–13]: $[\text{Al}(\text{opo})_3]$, $[\text{Si}(\text{opo})_3]\text{X}$ ($\text{X} = \text{Cl}, \text{FeCl}_4, \frac{1}{2}\text{SnCl}_6$), $[\text{Sn}(\text{opo})_3]_2 \cdot [\text{SnCl}_6]$, $[\text{Fe}(\text{opo})_3]$, $[\text{Cu}(\text{opo})_2]$, $[\text{Co}(\text{opo})_2]$ and $[\text{Co}(\text{opo})_3]$. Preparative and analytical data have been reported for the copper and cobalt complexes only. A partial optical resolution has been carried out on the silicon system [14]. This confirms the presence of the octahedral cation $[\text{Si}(\text{opo})_3]^+$, containing bidentate ligand.

The cobalt complexes have been characterised by nmr and electronic spectra and by room temperature magnetic moments [13]. Formation constants have been reported for complexes of opo with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) [15].

We have extended the coordination chemistry of Hopo by characterising a range of transition metal complexes, and we report X-ray powder diffraction, Mössbauer, infrared and electronic spectra on the complexes, together with magnetic data down to liquid nitrogen temperatures.

Results and Discussion

The complexes were all obtained from preparations in alcoholic media, and analytical data are given in Table I. Bidentate coordination of opo, the deprotonated ligand, was confirmed in the previously mentioned silicon(IV) complex and appears the most likely form in the others previously isolated. Bidentate coordination also seems likely for the complexes reported here, from a consideration of the stoichiometry of the complexes, and their likely coordination numbers, as ascertained by the physical measurements discussed below.

Infrared data for Hopo and complexes are given in Table II. Katritzky *et al.* [6] assigned $\nu(\text{NO})$ at 1110 cm^{-1} and $\nu(\text{CO})$ at 1655 cm^{-1} for Hopo in chloroform solution. Hopo is considered to exist

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TABLE I. Analytical Data.

Compound	Analyses %			
	Calculated/Found			
	C	H	N	M
1-hydroxy-2-pyridone (Hopo)	54.05	4.54	12.61	—
	53.74	4.36	12.42	—
Cu(opo) ₂	42.33	2.84	9.87	22.40 blue-green
	42.53	3.08	9.53	22.61
Cu(opo)NO ₃ , H ₂ O	23.68	2.38	11.04	25.05 bright green
	23.94	2.68	10.70	25.28
Cu(opo)Br, 0.5CH ₃ OH	24.51	2.24	5.20	23.57 yellow-brown
	24.59	1.89	5.18	23.31
Cu(opo)Cl	28.72	1.93	6.70	30.39 light green
	28.69	2.43	7.04	30.53
Ni(opo)Cl, 1.5H ₂ O	25.96	3.05	6.06	25.38 light green
	25.92	3.10	6.04	25.12
Co(opo)Cl, 1.5H ₂ O	25.94	3.05	6.05	25.45 light purple
	26.35	2.99	6.20	25.23
Fe(opo) ₃ , H ₂ O	44.57	3.49	10.40	13.81 bright red
	44.62	3.46	10.57	13.78

TABLE II. Infrared Spectral Data (cm⁻¹)^a.

Compound	$\nu(\text{CO})$	$\nu(\text{NO})$
Hopo ^b (chloroform solution)	1655 s	1110 w
Hopo (KBr disk)	1637 vs	1113 w
Hopo	1632 vs	1115 w
Cu(opo) ₂	1612 s	1182 vs
Cu(opo)NO ₃ ·H ₂ O	1621 mb	—
Cu(opo)Br, 0.5CH ₃ OH	1612 s	1183 vs
Cu(opo)Cl	1618 vs	1191 vs
Ni(opo)Cl, 1.5H ₂ O	1622 vs	1178 vs
Co(opo)Cl, 1.5H ₂ O	1622 vs	1181 vs
Fe(opo) ₃ , H ₂ O	1618 vs	1188 vs

^aMull spectra, unless otherwise indicated. ^bFrom reference [6].

mainly in the pyridone form (I). In keeping with this, the $\nu(\text{NO})$ frequency is considerably lower than for substituted pyridine N-oxides, in which it usually occurs at *ca.* 1200–1290 cm⁻¹ [1]. In Hopo complexes, as discussed in the previous paragraph, bidentate coordination is expected. Infrared data on the complexes are consistent with this. The $\nu(\text{CO})$ frequencies in the complexes are lower than in the free ligand, in agreement with carbonyl coordination. A strong new band occurs in the complexes at *ca.* 1180 cm⁻¹, and this band is assigned to $\nu(\text{NO})$. The frequency is similar to those for $\nu(\text{NO})$ bands in coordinated pyridine N-oxide ligands, and in complexes, M(pto)₂, of the ligand 1-hydroxy-2-pyridine-thione (Hpto, V), the sulfur analogue of Hopo [16].

TABLE III. Magnetic Data.

Complex	μ_{eff} (B.M.)		θ (K)*
	298 K	89 K	
Cu(opo) ₂	1.94	1.83	-15
Cu(opo)NO ₃ , H ₂ O	1.88	1.82	-5
Cu(opo)Br, 0.5CH ₃ OH	1.47	0.61	—
Cu(opo)Cl	1.84	1.91	+10
Ni(opo)Cl, 1.5H ₂ O	3.24	3.40	+18
Co(opo)Cl, 1.5H ₂ O	4.78	4.79	+6
Fe(opo) ₃ , H ₂ O	5.86	5.91	0

*Corresponds to θ in $\chi_{\text{M}} = C/(T - \theta)$.



(V) Hpto

Magnetic measurements (Table III) show that the complexes obey the Curie–Weiss law with small θ values, except for Cu(opo)Br, 0.5CH₃OH which is strongly antiferromagnetic. Reflectance spectra for the complexes are shown in Table IV.

A bis-chelate square planar structure is possible for Cu(opo)₂. Similar structures occur for bis-complexes with O,O ligands such as salicylaldehyde, acetylacetone and tropolone [17, 18]. Such square

TABLE IV. Reflectance Spectra.

Compound	Absorption Maxima ($\text{cm}^{-1} \times 10^{-3}$)
$\text{Cu}(\text{opo})_2$	13.8 sh, 15.8
$\text{Cu}(\text{opo})\text{NO}_3, \text{H}_2\text{O}$	11.3 sh, 13.7 sh, 14.8
$\text{Cu}(\text{opo})\text{Br}, 0.5\text{CH}_3\text{OH}$	10.3 sh, 12.3, 13.9 sh
$\text{Cu}(\text{opo})\text{Cl}$	11.1 sh, 14.3
$\text{Ni}(\text{opo})\text{Cl}, 1.5\text{H}_2\text{O}$	
Room Temperature	7.8 sh, 8.9; 13.9; 20.4 sh; 23.3
83 K	8.0 sh, 9.4; 14.0; 21.2 sh; 23.7
$\text{Co}(\text{opo})\text{Cl}, 1.5\text{H}_2\text{O}$	
Room Temperature	6.8 sh, 8.3; 15.3; 17.4, 19.0 sh, 19.9 sh
83 K	6.6, 8.5; 15.8; 17.7, 19.2 sh, 19.9 sh

TABLE V. Magnetic Data for $\text{Cu}(\text{opo})\text{Br}, 0.5\text{CH}_3\text{OH}$.

Temp. (K)	$10^6 \chi'_M$ (cgsu)	μ_{eff} (BM)
298	895	1.47
275	912	1.42
255	912	1.37
235	904	1.31
215	895	1.25
196	870	1.17
176	811	1.07
163	773	1.01
147	726	0.93
132	654	0.83
118	587	0.75
104	578	0.70
89	523	0.61

planar copper(II) complexes usually have absorption bands at *ca.* 15,000 and 17,500 cm^{-1} [18–21]. $\text{Cu}(\text{opo})_2$ has one band at *ca.* 15,800 cm^{-1} , with a shoulder at 13,800 cm^{-1} , but no trace of a band in the 17–18,000 cm^{-1} region. A five or six-coordinate oxygen-bridged structure is, therefore, considered more likely for $\text{Cu}(\text{opo})_2$. Five-coordinate complexes of type $[\text{Cu}(\beta\text{-diketone})_2\text{pyridine}]$ have a single band at *ca.* 15,000 cm^{-1} [18]. Also, $\text{Cu}(\omega\text{-nitroacetophenone})_2$ has a six-coordinate structure produced by association of bis-chelate molecules via a second O on the NO_2 groups, and this complex has a main reflectance band at 16,000 cm^{-1} , with a shoulder at 13,000 cm^{-1} [22]. Many other CuO_5 and CuO_6 systems have spectra of this type, similar to that of $\text{Cu}(\text{opo})_2$ [21].

The complex $\text{Cu}(\text{opo})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ has nitrate infrared absorptions as follows: ν_3 , 1498, 1253 (vsb); ν_2 , 808 (m); and ν_1 , 1016 (m) cm^{-1} , indicating biden-

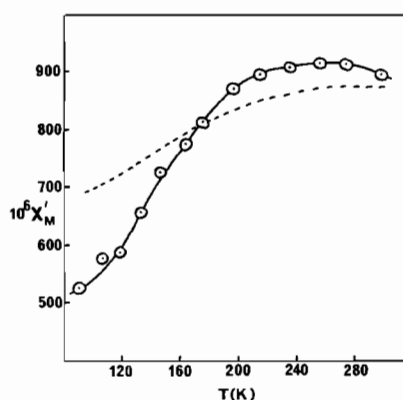


Fig. 1. The temperature dependence of $10^6 \chi'_M$ for the complex $\text{Cu}(\text{opo})\text{Br}, 0.5\text{CH}_3\text{OH}$. Experimental points are indicated by circles. The full line represents the best fit using equation (ii) (D_{2d} tetramer) and the broken line is the best fit using equation (iv) (Ising linear polymer). The values of the parameters are given in Table VI.

tate nitrate [23]. The compound could have a square-planar structure, or coordination by water could produce a five-coordinate structure. The reflectance spectrum has a band at 14,800 cm^{-1} with no absorption at *ca.* 17–18,000 cm^{-1} . For the reasons discussed above with $\text{Cu}(\text{opo})_2$, the reflectance spectrum supports a five-coordinate structure, or even a six-coordinate structure, which would be possible if bridging opo were present.

The complex $\text{Cu}(\text{opo})\text{Br}, 0.5\text{CH}_3\text{OH}$ is markedly antiferromagnetic, suggesting either an oxygen or bromine-bridged complex. Such magnetic interaction is known for copper(II) complexes with bridging *N*-oxide, bridging phenol or bridging bromine [1, 24, 25]. The magnetic data for $\text{Cu}(\text{opo})\text{Br}, 0.5\text{CH}_3\text{OH}$, measured down to 89 K, are shown in Table V. The data have been fitted to various models. The equations for the models are listed in the experimental section. It was necessary to allow for a small

TABLE VI. Magnetic Data for Cu(opo)Br, 0.5CH₃OH and Best Fits^a to Various Polynuclear Models.

Model (equation no.) ^b	g	J (or J ₁) (cm ⁻¹)	J ₂ (cm ⁻¹)	Proportion of Monomer	$\left\{ \frac{\sum (\chi_{\text{obs}} - \chi_{\text{calc}})^2}{\sum (\chi_{\text{obs}})^2} \right\}^{1/2}$	SE ^c
Dimer (1)	2.205	-161	-	0.072	0.012	0.007
Distorted tetrahedron of coppers (2)	2.025	-160	+54	0.073	0.012	0.007
Regular tetrahedron of coppers (3)	2.40	-141	-	0.057	0.066	0.045
Ising linear polymer (4)	2.40	-202.5	-	0.0	0.101	0.053
Heisenberg chain of coppers with infinite spin (5)	2.40	-200.5	-	0.0	0.161	0.090

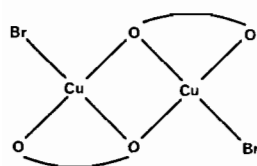
^aBecause of the large number of parameters, least squares procedures did not work well. The best fits were obtained by a mapping routine, minimising the value of $\sum |x_{\text{obs}} - x_{\text{calc}}| / \sum x_{\text{obs}}$. ^bEquations are listed in the Experimental Section. ^cS. E. is the standard error expression, $\{ \sum [\mu_{\text{eff}}(\text{obs}) - \mu_{\text{eff}}(\text{calc})]^2 / (NP - k) \}^{1/2}$, where k is the number of parameters used to fit the NP data points (Ginsberg *et al.*, *Inorg. Chem.*, 11, 2884 (1972)).

proportion of monomer. Trimeric structures were excluded, because the moment per copper drops below 1.0 B.M., the theoretical minimum for trimeric copper(II) systems [26]. Fitting parameters are listed in Table VI, and some calculated susceptibilities are illustrated in Fig. 1.

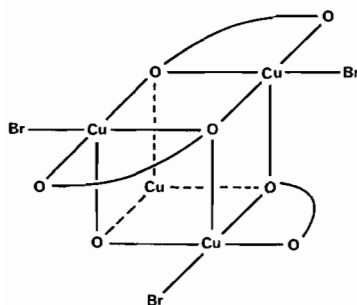
Good fits, within experimental error, could only be obtained for:

(a) a dimer structure (equation 1), possibly as in (VI).

(b) a tetramer structure involving a distorted (D_{2d}) cluster of coppers (equation 2); this could be produced from two dimers associated via out of plane bridging as in (VII).



(VI)



(VII)

The planar dimer structure (VI) is not favoured, because Cu(opo)Br,0.5CH₃OH has its main

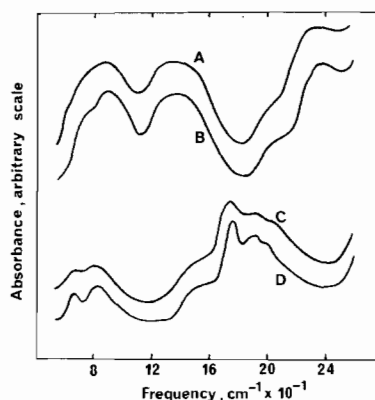


Fig. 2. Diffuse reflectance spectra. Ni(opo)Cl, 1.5H₂O: at room temperature (A) and liquid nitrogen temperature (B); Co(opo)Cl, 1.5H₂O: at room temperature (C) and liquid nitrogen temperature (D).

reflectance band at 12,300 cm⁻¹, which seems too low in frequency for square planar coordination. A tetrahedral distortion of the bonding of the copper atoms in (VI) could lower the absorption frequency [22, 27], but there are no structural features in Cu(opo)Br,0.5CH₃OH which would favour such a distortion. The complex is, therefore, most likely five- or six-coordinate, with dimeric units associated into tetramers, as in (VII).

The complex Cu(opo)Cl, whose μ_{eff} increases slightly with decreasing temperature must have either chlorine or oxygen-bridging to achieve four-coordination. A planar dimeric structure is unlikely, since this usually leads to strong antiferromagnetism. Association of dimers into a cubane structure similar to (VII) may occur, since this can lead to very weak overall interaction, in some cases [28]. The electronic spectra of few Cu^{II}O_xCl_y systems are avail-

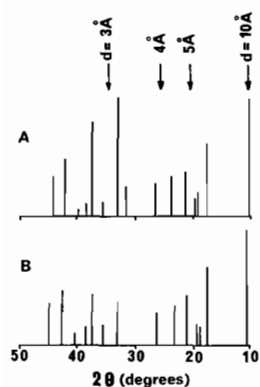
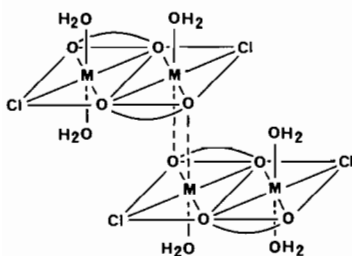


Fig. 3. X-ray powder diffraction patterns for (A) Ni(opo)Cl, 1.5H₂O and (B) Co(opo)Cl, 1.5H₂O, using CoK_α radiation.

able, but the spectrum of Cu(opo)Cl is somewhat similar to that of Cu(dimethylsulfoxide)₂Cl₂ (ν_{\max} 12,900; 14,900 cm⁻¹) which has a CuO₂Cl₃ chromophore [29].

The electronic spectrum of Ni(opo)Cl, 1.5H₂O (Fig. 2) suggests a six-coordinate structure and contains the three bands $\nu_1(^3T_{2g} \leftarrow ^3A_{2g})$, $\nu_2(^3T_{1g} \leftarrow ^3A_{2g})$ and $\nu_3(^3T_{1g}(P) \leftarrow ^3A_{2g})$ of octahedral nickel(II). The nickel(II) environment is somewhat lower than O_h, since a slight shoulder, at ca. 8000 cm⁻¹, is present on the ν_1 band at room temperature, and this is almost resolved into a second component at 83 K. This lower symmetry is in keeping with the dissimilar donor atoms available for the nickel(II) ion. Using the centre of gravity for the ν_1 , ν_2 and ν_3 absorptions (8,500; 13,800 and 23,300 cm⁻¹, respectively), the theoretical values of 13,850 and 23,250 cm⁻¹ are calculated for the ν_2 and ν_3 bands respectively, indicating only a small departure from an octahedral model [30]. In order to produce six-coordination, bridging is necessary and one possible structure is shown in (VIII).



(VIII)

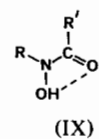
Magnetic measurements on Ni(opo)Cl, 1.5H₂O show a rise in μ_{eff} of 0.16 B.M. on cooling to 89 K, which may be associated with weak ferromagnetic interaction caused by the bridged structure.

The X-ray powder pattern of Co(opo)Cl, 1.5H₂O (Fig. 3) suggests that it is isostructural with its nickel(II) analogue. The reflectance spectrum of the cobalt-

(II) complex (Fig. 2) indicates a distorted six-coordinate environment, since the ν_1 and ν_3 bands (the $^4T_{2g} \leftarrow ^4T_{1g}$ and $^4T_{1g}(P) \leftarrow ^4T_{1g}$ transitions, respectively in O_h symmetry) have shoulders or components at room temperature, more clearly resolved at liquid nitrogen temperature [31–33]. Similar spectra occur for other distorted octahedral cobalt(II) complexes.

The magnetism of the cobalt(II) complex differs from that of octahedral monomeric cobalt(II) complexes, since the latter usually [25, 34] have *theta* values of ca. -10 to -40 K, whereas Co(opo)Cl, 1.5H₂O has a small positive *theta* value of 6 K. This may be due to ferromagnetic exchange in Co(opo)Cl, 1.5H₂O, produced by a bridged structure, as found with Ni(opo)Cl, 1.5H₂O and Cu(opo)Cl.

The complex Fe(opo)₃, H₂O has no detectable d-d bands in its reflectance spectrum, and is high-spin. The Mössbauer spectrum shows isomer shifts at room temperature, and liquid nitrogen temperature, of 0.58 and 0.52 mm s⁻¹, respectively, similar to other Fe¹¹¹O₆ chromophores [35, 36]. No detectable quadrupole splitting is present, suggesting a regular octahedral chromophore. In contrast, the tris-complexes of iron(III) with hydroxamic acids (IX), and with 1-hydroxy-2-pyridinethione (V), have a Mössbauer quadrupole splitting, because of the unsymmetrical ligand field produced by the chelates [37].



(R, R' = H, alkyl or aryl)

Thus the single line spectrum of Fe(opo)₃, H₂O indicates the similar donor capacity of the oxygen atoms of opo.

We have shown that opo readily gives species of the type M(opo)X, containing one chelate and one anion. This is unusual for uninegative O,O ligands, which usually yield only [Mⁿ⁺(chel)_n] complex species [38].

Experimental

1-Hydroxy-2-pyridone

This was prepared by Wagner and Pischel's method [39], but starting from 2-chloropyridine N-oxide [40], instead of 2-bromopyridine N-oxide.

Preparation of Complexes

All complexes were dried under vacuum over phosphorus pentoxide.

Cu(opo)₂

The ligand (1.15 g) was dissolved in warm alcohol (30 ml) and added to a boiling alcohol (70 ml) solution of copper(II) acetate monohydrate (1.0 g). The complex was deposited immediately as a dark blue-green powder.

Cu(opo)NO₃, H₂O

Copper(II) nitrate trihydrate (2.1 g) in alcohol (20 ml) was added to a boiling solution of the ligand (1.0 g) in alcohol (20 ml). The resulting solution was concentrated to about 25 ml and left to stand for 2 days. Petroleum ether (20 ml, 60–80 °C) was added slowly to the solution. Green crystals were deposited after a few days.

Cu(opo)Br, 0.5CH₃OH

The ligand (0.87 g) was dissolved in boiling alcohol (20 ml) and added to a boiling methanol solution (40 ml) of anhydrous copper(II) bromide (1.76 g). The solution was warmed for 15 min and then filtered and petroleum ether (60–80 °C, 30 ml) was slowly added and the solution left to stand for several days, whereupon the complex was deposited.

Cu(opo)Cl

The ligand (1.1 g) was dissolved in boiling alcohol (30 ml). This solution was added to a boiling alcohol (30 ml) solution of copper(II) chloride dihydrate (1.63 g). The resulting solution was allowed to cool, whereupon a light green powder was deposited.

Ni(opo)Cl, 1.5H₂O and Co(opo)Cl, 1.5H₂O

The ligand (1.08 g) was dissolved in warm alcohol (20 ml) and added to a warm alcohol (20 ml) solution of nickel(II) chloride hexahydrate (2.33 g). The solution was concentrated to about 20 ml and petroleum ether (60–80 °C, 20 ml) was added. Upon leaving the solution to stand for several days, light green flakes were deposited. The cobalt(II) complex was prepared in a similar manner.

Fe(opo)₃, H₂O

The ligand (1.0 g) was dissolved in boiling alcohol (30 ml) and added to a warm alcohol (30 ml) solution of anhydrous iron(III) chloride (1.1 g) in alcohol (30 ml). The solution was warmed for 10 min. After the solution had cooled, the red complex was deposited.

Analyses

The carbon, hydrogen and nitrogen analyses were determined by Dr. E. Challen and Mr. J. Sussman of the Microanalytical Laboratory, University of New South Wales, and by the Australian Microanalytical Service, Melbourne. Metal analyses were made by standard gravimetric procedures.

Physical Measurements

Infrared spectra were obtained on compounds mullied in paraffin or halocarbon, or compressed in potassium bromide disks, using Perkin-Elmer 337 or 521 spectrophotometers.

The electronic diffuse reflectance spectra were measured on a Zeiss PMQII spectrophotometer with an RA3 reflectance attachment. Spectra at liquid nitrogen temperature were obtained by placing the samples, spread on filter paper, in contact with the base of a brass vessel containing liquid nitrogen.

X-ray powder diffraction spectra were obtained with CoK_α radiation on a Philips 100X-ray powder diffractometer.

Mössbauer spectra were obtained on an instrument described by Tennant [41]. A ⁵⁷Co source was used, and the instrument was calibrated using sodium nitroprusside.

Magnetic measurements to liquid nitrogen temperatures were made on a Newport variable temperature Gouy balance.

Susceptibility Equations

The following equations were used to fit the magnetic data of Cu(opo)Br, 0.5CH₃OH. A proportion of monomer is included in each case. Details of the fits are given in Table VI.

i) Bleaney Bowers equation for a dimer [42]

$$\chi_M = (1 - m) \left(\frac{N\beta^2 g^2}{kT} \right) [3 + \exp(-2J/kT)]^{-1} + \text{(per Cu atom)} + m \frac{(0.448)}{T} + N\alpha \quad (1)$$

Here *m* is the proportion of monomer. The temperature independent paramagnetism, *Nα*, is taken as 60 × 10⁻⁶ cgsu per copper in each equation. The remaining symbols have their usual meaning.

ii) Tetramer involving a distorted (D_{2d}) cluster of coppers, possibly produced from two dimers associated via out of plane bridging [43, 44], as in structure (VI).

$$\chi_M = (1 - m) \left(\frac{N\beta^2 g^2}{12kT} \right) \text{(per Cu atom)} + \frac{[12 + 6x^2y^{-2} + 30x^2y^2]}{[6 + x^{-2} + x^2y^{-4} + 3x^2y^{-2} + 5x^2y^2]} + \frac{m(0.448)}{T} + N\alpha \quad (2)$$

where *x* = exp(*J*₁/*kT*), *y* = exp(*J*₂/*kT*)

In this equation, *J*₁ is the exchange constant for in plane interaction within each dimer unit, and *J*₂

is the constant for out of plane interaction between dimer units.

iii) Regular tetrahedral cluster of coppers [43]

$$\chi_M = (1 - m) \left(\frac{N\beta^2 g^2}{12kT} \right) \frac{[30 + 18\exp(-4J/kT)]}{[5 + 9\exp(-4J/kT) + 2\exp(-6J/kT)]} + \frac{m(0.448)}{T} + N(\alpha) \quad (3)$$

iv) Ising equation for linear polymer of coppers [45]

$$\chi_M = (1 - m) \left(\frac{N\beta^2 g^2}{12kT} \right) \frac{[e^{4K} + (2 + K^{-1})e^{2K} - K^{-1}e^{-2K} + 5]}{[e^{2K} + e^{-2K} + 2]} + \frac{m(0.448)}{T} + N(\alpha) \quad (4)$$

where $K = J/kT$.

v) Heisenberg chain of coppers, with infinite spin [46]

$$\chi_M = (1 - m) \left(\frac{N\beta^2 g^2}{4kT} \right) \frac{(1 + u)}{(1 - u)} + \frac{m(0.448)}{T} + N\alpha \quad (5)$$

where $u = \coth(3J/2kT) - 2kT/3J$.

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