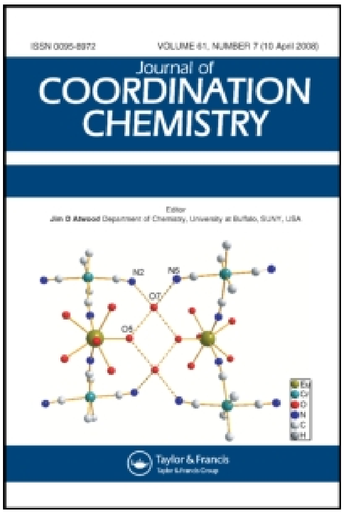

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COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES WITH *N,N'*-BIS(2-*N,N*-DIMETHYLAMINOETHYL)PYRIDINE-2,6-DICARBOXAMIDE 1-OXIDE. BINUCLEATING BEHAVIOUR BY A DEPROTONATED PYRIDINE *N*-OXIDE LIGAND

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COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES WITH *N,N'*-BIS(2-*N,N*-DIMETHYLAMINOETHYL)PYRIDINE-2,6-DICARBOXAMIDE 1-OXIDE. BINUCLEATING BEHAVIOUR BY A DEPROTONATED PYRIDINE *N*-OXIDE LIGAND

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New copper(II), nickel(II), and cobalt(II) complexes are described with the potentially binucleating pyridine *N*-oxide ligand *N,N'*-bis(2-*N,N*-dimethylaminoethyl)pyridine-2,6-dicarboxamide 1-oxide (medpco). Electronic spectra and X-ray powder diffraction measurements indicate that metal complexes of the type $M(medpco)Hal_2(H_2O)_x$ (Hal = Cl, Br) are five-coordinate. Monomeric structures are proposed with ONN-bonded ligand and coordinated halide. This is analogous to the coordination to one of the coppers in the previously reported X-ray structure of $Cu_2(medpco)Cl_4$. Complexes of the type $M'_2(medpco\text{-}2H)Hal_2(H_2O)_x$ ($M' = Ni, Co$), involving deprotonated ligand, are reported. These appear to have *N*-oxide-bridged structures, involving binucleating ligand, analogous to the previously reported X-ray structure of $Cu_2(medpco\text{-}2H)Cl_2$. Variable temperature magnetic data for the complexes are discussed.

Keywords: Pyridine *N*-oxide complexes; *N*-oxide bridging;
binucleating ligand; nickel(II); cobalt(II)

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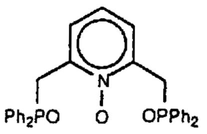
INTRODUCTION

There has been extensive work on binucleating ligands involving bridging phenolate,[1] enolate,[2] and diazine groups.[3] In contrast, much less work on binucleating pyridine *N*-oxide ligands has been reported. No binucleating behaviour has been reported for the potentially binucleating pyridine *N*-oxide ligand 2,6-bis((diphenylphosphino)methyl)pyridine *N,P,P'*-trioxide (1).[4] The deprotonated form of the ligand 2,6-pyridinedicarboxylic acid 1-oxide (H_2dpco_2o, **2**) acts as a binucleating ligand in the polymeric compound, $[Mn(dpco_2o)H_2O]_n$.[5] On the other hand, binucleating ligand is absent in $[UO_2(dpco_2o)(H_2O)_2]_2$[6] and $[Cu(dpco_2o)CH_3OH)(py)]_2$ (py= pyridine)[7] and there is no evidence, at present, for binucleating behaviour by this ligand with other metals.[5,8] Recently, Blake *et al.* studied a macrocyclic ligand derived from the reaction of 2,6-pyridinedicarboxaldehyde 1-oxide with ethylenediamine. The ligand acts as a binucleating ligand, yielding a series of di-metal *N*-oxide-bridged complexes.[9]



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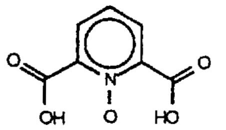
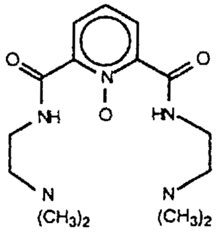


(**2**, H_2dpco_2o)



(**3**, medpco)

We have been investigating the potentially binucleating ligand medpco (**3**).[10,11] In a preliminary communication, we showed that the neutral ligand does not function as a binucleating ligand in the complex $Cu_2(medpco)Cl_4$, whose X-ray structure determination shows that chloride bridging occurs between the copper(II) ions.[10] However, we then showed that the deprotonated ligand does act as a binucleating ligand in a series of copper(II) complexes of the type $Cu_2(medpco\text{-}2H)X_2$.[11]

In this paper we report an extension of this work to complexes of nickel(II) and cobalt(II) and also additional new complexes of copper(II). Examples of binucleating behaviour by deprotonated medpco are observed with nickel(II) and cobalt(II).

EXPERIMENTAL

Preparations

All metal complexes were dried in vacuum over phosphorus pentoxide.

$Cu_2(medpco)Cl_4$

A boiling solution of medpco[11] (1.0 g, 3.1 mmol) in absolute ethanol (30 mL) was added to a boiling solution of $CuCl_2 \cdot 2H_2O$ (1.2 g, 7.0 mmol) in absolute ethanol (60 mL) and 2,2-dimethoxypropane (15 mL). Dark green crystals formed on cooling. Yield 1.7 g, 93%. *Anal.* Calcd. for $Cu_2C_{15}H_{25}N_5O_3Cl_4$(%): C, 30.4; H, 4.3; N, 11.8. Found: C, 30.7; H, 4.5; N, 11.7.

$Cu_2(medpco)Br_4$

A hot filtered solution of $CuBr_2$ (3.00 g, 13.4 mmol) in absolute ethanol (100 mL) and triethylorthoformate (5 mL) was added to a hot solution of medpco (1.10 g, 3.4 mmol) in absolute ethanol (60 mL). The black solution was left to cool slowly. Black crystals deposited and were collected and washed thoroughly with cold absolute ethanol, until the washings were colourless. Yield 2.5 g, 95%. *Anal.* Calcd. for $Cu_2C_{15}H_{25}N_5O_3Br_4$(%): C, 23.4; H, 3.3; N, 9.1; Cu, 16.5. Found: C, 23.6; H, 3.3; N, 9.0; Cu, 16.3.

$Cu(medpco)Cl_2$

A boiling solution of medpco (1.0 g, 3.1 mmol) in absolute ethanol (15 mL) was added to a boiling solution of $CuCl_2 \cdot 2H_2O$ (0.52 g, 3.1 mmol) in absolute ethanol (20 mL) and 2,2-dimethoxypropane (6 mL). Green crystals formed on cooling. Yield 1.2 g, 82%. *Anal.* Calcd. for $CuC_{15}H_{25}N_5O_3Cl_2$(%): C, 39.4; H, 5.5; N, 15.3. Found: C, 39.3; H, 5.3; N, 15.2.

$Cu(medpco)Br_2 \cdot H_2O$

A hot solution of $CuBr_2$ (0.69 g, 3.1 mmol) in absolute ethanol (50 mL) and triethylorthoformate (5 mL) was added to a hot solution of medpco (1.0 g, 3.1 mmol) in absolute ethanol (50 mL). A dark green solution formed and a bright green precipitate deposited almost immediately. The crystals were collected and washed with absolute ethanol. Yield 1.4 g, 80%. *Anal.* Calcd. for $CuC_{15}H_{27}N_5O_4Br_2$(%): C, 31.9; H, 4.8; N, 12.4; Cu, 11.3. Found: C, 31.8; H, 4.9; N, 12.5; Cu, 11.0.

$Ni(medpco)Cl_2$

The preparation resembled that of $Cu(medpco)Cl_2$, but using 10 mL of 2,2-dimethoxypropane, giving yellow crystals. Yield 1.3 g, 93%. *Anal.* Calcd. for $NiC_{15}H_{25}N_5O_3Cl_2$(%): C, 39.8; H, 5.6; N, 15.5. Found: C, 39.8; H, 5.7; N, 15.2.

$Ni(medpco)Br_2$

A hot solution of $NiBr_2 \cdot 3H_2O$ (1.7 g, 6.2 mmol) in absolute ethanol (50 mL) and triethylorthoformate (10 mL) was added to a hot solution of medpco (1.0 g, 3.1 mmol) in absolute ethanol (50 mL). A yellow-orange precipitate formed immediately and was collected and washed with absolute ethanol. Yield 1.6 g, 95%. *Anal.* Calcd. for $NiC_{15}H_{25}N_5O_3Br_2$(%): C, 33.3; H, 4.7; N, 12.9; Ni, 10.8. Found: C, 33.2; H, 4.7; N, 12.8; Ni, 10.5.

$Co(medpco)Cl_2 \cdot H_2O$

A hot solution of $CoCl_2 \cdot 6H_2O$ (0.74 g, 3.1 mmol) in absolute ethanol (50 mL) and triethylorthoformate (10 mL) was added to a hot solution of medpco (1.0 g, 3.1 mmol) in absolute ethanol (50 mL). A green solution formed and a green precipitate deposited on cooling. This was collected and washed with absolute ethanol. Yield 1.2 g, 82%. *Anal.* Calcd. for $CoC_{15}H_{27}N_5O_4Cl_2$(%): C, 38.2; H, 5.8; N, 14.9; Co, 12.5. Found: C, 38.0; H, 5.8; N, 14.7; Co, 12.1.

$Co(medpco)Br_2 \cdot H_2O$

The preparation resembled that of $Co(medpco)Cl_2 \cdot H_2O$, giving a green precipitate. Yield 1.6 g, 92% *Anal.* Calcd. for $CoC_{15}H_{27}N_5O_4Br_2$(%): C, 32.2; H, 4.9; N, 12.5; Co, 10.5. Found: C, 31.9; H, 4.9; N, 12.3; Co, 10.2.

$Ni_2(medpco\text{-}2H)Cl_2 \cdot 2H_2O$

A solution of triethylamine (0.70 g, 6.9 mmol) in absolute ethanol (5 mL) was added to a hot solution of medpco (1.0 g, 3.1 mmol) in absolute ethanol (45 mL). A hot solution of $NiCl_2 \cdot 6H_2O$ (1.6 g, 6.7 mmol) in absolute ethanol (50 mL) and triethylorthoformate (5 mL) was immediately added. A yellow solution formed, was seeded and left to stand overnight. The fine yellow precipitate was collected and washed thoroughly with absolute ethanol.

Yield 1.0 g, 59%. *Anal.* Calcd. for $Ni_2C_{15}H_{27}N_5O_5Cl_2$(%): C, 33.0; H, 5.0; N, 12.8. Found: C, 33.3; H, 4.6; N, 13.0.

Ni_2(medpco-2H)$Br_2 \cdot 2H_2O$

A solution of triethylamine (0.70 g, 6.9 mmol) in absolute ethanol (5 mL) was added to a hot solution of medpco (1.0 g, 3.1 mmol) in absolute ethanol (45 mL). A hot solution of $NiBr_2 \cdot 3H_2O$ (1.9 g, 7.0 mmol) in absolute ethanol (50 mL) and triethylorthoformate (10 mL) was immediately added. A honey coloured solution formed and was seeded and left to stand overnight. The dark yellow precipitate was collected and washed thoroughly with absolute ethanol. Yield 1.4 g 71%. *Anal.* Calcd. for $Ni_2C_{15}H_{27}N_5O_5Br_2$(%): C, 28.4; H, 4.3; N, 11.0; Ni, 18.5. Found: C, 28.4; H, 4.3; N, 11.0; Ni, 18.7.

Co_2(medpco-2H)$Cl_2 \cdot H_2O$

The preparation resembled that of Ni_2(medpco-2H)$Cl_2 \cdot 2H_2O$, giving a grey-green precipitate, without the need for seeding. Yield 1.4 g, 86%. *Anal.* Calcd. for $Co_2C_{15}H_{27}N_5O_4Cl_2$(%): C, 34.1; H, 4.8; N, 13.3; Co, 22.3. Found: C, 34.0; H, 4.9; N, 13.1; Co, 22.3.

Co_2(medpco-2H)Br_2

The preparation resembled that of Ni_2(medpco-2H)$Br_2 \cdot 2H_2O$, but using 2.5 g (7.6 mmol) of $CoBr_2 \cdot 6H_2O$. An almost immediate dark green precipitate was obtained, without the need for seeding. Yield 1.8 g, 97%. *Anal.* Calcd. for $Co_2C_{15}H_{23}N_5O_3Br_2$(%): C, 30.1; H, 3.9; N, 11.7; Co, 19.7. Found: C, 30.2; H, 4.1; N, 11.4; Co, 19.6.

Analyses and Physical Measurements

These were as previously described.[12]

RESULTS AND DISCUSSION

Metal complexes with neutral and depronated medpco are listed in Table I with data for reflectance spectra. Magnetic data are given in Table II.

TABLE I Diffuse reflectance spectra for the complexes

Compound	*Temperature* (K)	*Absorption maxima*[a,b] ($cm^{-1} \times 10^{-3}$)
$Cu_2(medpco)Cl_4$	298	7–17br
	80	9.0, 12.1, 15.7
$Cu_2(medpco)Br_4$	298	8.0sh, 8–26s,br
$Cu(medpco)Cl_2$	298	14.0
$Cu(medpco)Br_2 \cdot H_2O$	298	13.7
	80	10.4sh, 14.0
$Ni(medpco)Cl_2$	298	13.5br
	80	11.1vw, 13.6
$Ni(medpco)Br_2$	298	10.8sh, 13.2
	80	9.2sh, 11.0sh, 13.7
$Co(medpco)Cl_2 \cdot H_2O$	298	6.9sh, 8.0, 12.6w, 16.0
	80	6.8sh, 8.3, 12.9w, 16.2
$Co(medpco)Br_2 \cdot H_2O$	298	6.9sh, 7.9, 12.4w, 16.0
	80	7.0sh, 8.1, 12.9w, 16.0
$Ni_2(medpco\text{-}2H)Cl_2 \cdot 2H_2O$	298	10.4sh, 14.0
	80	10.3w, 14.2
$Ni_2(medpco\text{-}2H)Br_2 \cdot 2H_2O$	298	9.6sh, 13.4
	80	9.6sh, 10.9sh, 13.7
$Co_2(medpco\text{-}2H)Cl_2 \cdot H_2O$	298	6.4, 12.3, 16.4
	80	6.6, 8.4w, 12.6, 16.3
$Co_2(medpco\text{-}2H)Br_2$	298	6.7, 9.0vw, 12.4w, 16.1
	80	6.6, 8.2, 12.7, 16.0, 17.0sh

[a] Sh = shoulder, br = broad, w = weak, v = very. [b] Strong ligand/charge transfer absorption commences at *ca.* 20 000 cm^{-1} and extends over the higher frequency region.

TABLE II Magnetic data for the complexes

Compound	μ_{eff} (BM)		θ (K)[a]
	305 K	89 K	
$Cu_2(medpco)Cl_4$	1.85	1.90	+8
$Cu_2(medpco)Br_4$	1.82	1.91	+14
$Cu(medpco)Cl_2$	1.91	1.85	−8
$Cu(medpco)Br_2 \cdot H_2O$	1.83	1.82	+1
$Ni(medpco)Cl_2$	3.29	3.20	−9
$Ni(medpco)Br_2$	3.29	3.21	−6
$Co(medpco)Cl_2 \cdot H_2O$	4.88	4.71	−9
$Co(medpco)Br_2 \cdot H_2O$	4.99	4.84	−8
$Ni_2(medpco\text{-}2H)Cl_2 \cdot 2H_2O$	3.20	3.20	−2
$Ni_2(medpco\text{-}2H)Br_2 \cdot 2H_2O$	3.06	2.96	−10
$Co_2(medpco\text{-}2H)Cl_2 \cdot H_2O$	4.52	4.18	−22
$Co_2(medpco\text{-}2H)Br_2$	4.46	4.02	−33

[a] θ is the Weiss Constant, where $\chi'_M = c/(T-\theta)$.

Complexes with Neutral Medpco

Attempts to obtain 2 : 1 complexes with neutral medpco were successful only with the complexes $Cu_2(medpco)Hal_4$, all other complexes having 1 : 1 compositions. We earlier reported the X-ray structure of $Cu_2(medpco)Cl_4$ in a

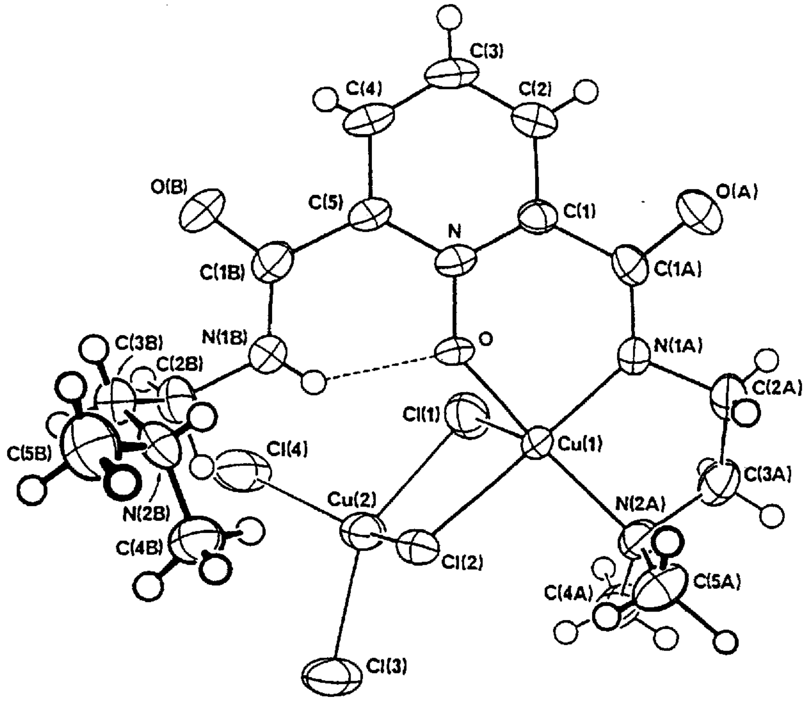


FIGURE 1 Structure of $Cu_2(medpco)Cl_4$.

preliminary communication.[10] The structure is shown in Figure 1, and some features are summarised as a background to the work reported in this paper. In $Cu_2(medpco)Cl_4$, the neutral ligand medpco is not binucleating but coordinates as an ONN donor to one copper, Cu(1). The ONN coordination involves the *N*-oxide oxygen, and the amide and tertiary nitrogens on 'one side' of the ligand molecule. The coordinated amide nitrogen, N(1A), is deprotonated, the amide hydrogen being transferred to the uncoordinated tertiary amine nitrogen N(2B), on the 'other side' of the ligand, in an internal deprotonation. The coordination to Cu(1) is five-coordinate $ONNCl_2$, since Cu(1) is also coordinated by two chlorides. These chlorides act as bridges to the second copper, Cu(2), which is located well away from the second ligand donor site. The coordination to Cu(2) is flattened tetrahedral, being completed by two terminal chlorides.

We earlier reported the reflectance electronic spectrum of $Cu_2(medpco)Cl_4$ but without assignments, which we now give.[10] The spectrum contains a broad asymmetric band over the range 7000–17 000 cm^{-1} (Table I). At liquid nitrogen temperature, this is resolved into bands at 9000, 12 100 and 15 700 cm^{-1}. The bands at 9000 and 12 100 cm^{-1} are assigned to Cu(2), with a '$CuCl_4$' structure, and similar bands are found for the distorted tetrahedral '$CuCl_4$' species in $[AsPh_4]_2[Cu_2Cl_6]$.[13] The remaining band in $Cu_2(medpco)Cl_4$ at 15 700 cm^{-1} is assigned to the five-coordinate Cu(1) which has $ONNCl_2$ coordination. A single band at *ca.* 14 000 cm^{-1} is found for the 1 : 1 $Cu(medpco)Hal_2$ complexes discussed later.

The new 2 : 1 copper bromide complex $Cu_2(medpco)Br_4$ is black. Its reflectance spectrum contains a shoulder at *ca.* 8000 cm^{-1} and then intense absorption over the rest of the higher frequency region of the spectrum. The high intensity is probably due to charge-transfer absorption in the visible region. Such low frequency charge-transfer absorption is known in some compounds containing the $[CuBr_4]^{2-}$ ion,[14,15] so it seems that $Cu_2(medpco)Br_4$ may contain a '$CuBr_4$' entity produced by bromide bridging in a structure similar to that of $Cu_2(medpco)Cl_4$.

The magnetism of $Cu_2(medpco)Br_4$ indicates weak ferromagnetism ($\theta = +14$ K) and the slight variation of μ_{eff} ($\theta = +8$ K)in $Cu_2(medpco)Cl_4$ is consistent with this (Table II). Ferromagnetism is found in some cases of halide-bridged copper(II) complexes.[13,16]

The remaining complexes with neutral medpco are new and have 1 : 1 stoichiometry. In the structure of $Cu_2(medpco)Cl_4$ (Figure 1), the medpco acts as an ONN donor to one copper, with the second coordination site being blocked by hydrogen bonding from the uncoordinated amide hydrogen to the *N*-oxide oxygen. Similar ONN coordination seems likely in the 1 : 1 complexes with neutral medpco discussed next.

The reflectance spectra of the 1 : 1 cobalt(II) and nickel(II) halide complexes indicate five-coordinate structures (Table I, Figure 2). The spectra of the $Ni(medpco)Hal_2$ complexes in the 7000–17 000 cm^{-1} region contain a single asymmetrical band, rather than the two bands associated with octahedral nickel(II). This is characteristic of many five-coordinate nickel(II) complexes, resembling, for example, the spectra of the five-coordinate complexes $Ni(Me_5dien)Hal_2$ (Me_5dien = bis(2-dimethylaminoethyl)methylamine).[14,17,18] Likewise, in the spectra of the 1 : 1 cobalt(II) halide complexes, the presence of a band at *ca.* 12 500 cm^{-1}, in addition to bands at *ca.* 8000 and 16 000 cm^{-1}, is typical of five-coordinate cobalt(II).[14,17,19] The spectra resemble the spectrum of five-coordinate β-$Co(paphy)Cl_2$-(paphy = 2-pyridinecarboxaldehyde 2′-pyridinylhydrazone).[19] Five-coordination is readily produced by ONN coordination by medpco and terminal halide coordination. X-ray powder diffraction patterns show that the nickel(II) and cobalt(II) halide complexes are all isostructural.

The 1 : 1 copper(II) halide complexes with neutral medpco are probably also five-coordinate, because the X-ray powder patterns are similar to those

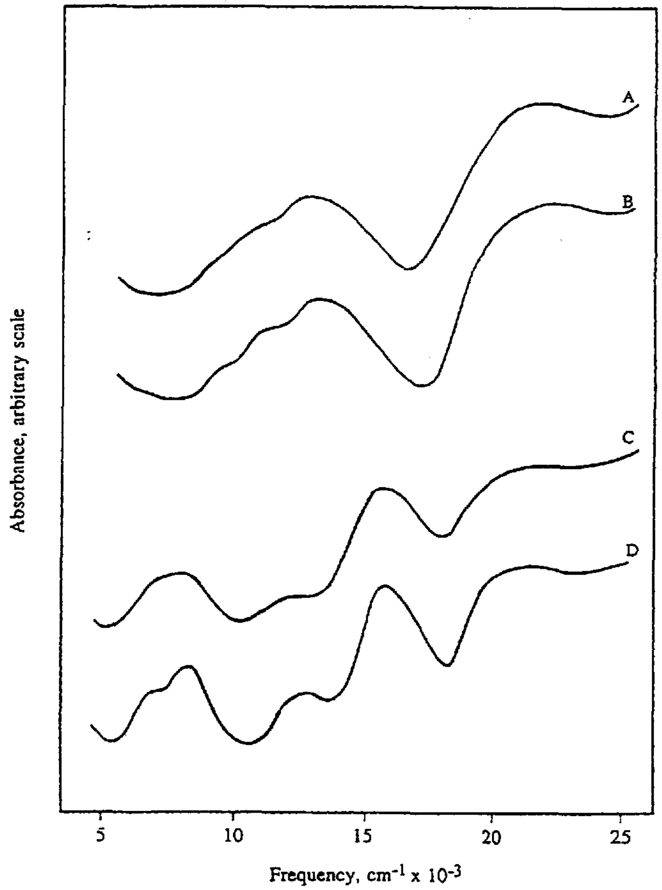


FIGURE 2 Diffuse reflectance spectra: Ni(medpco)Br_2 at room temperature (A) and liquid nitrogen temperature (B); Co(medpco)$Br_2 \cdot H_2O$ at room temperature (C) and liquid nitrogen temperature (D).

for the corresponding nickel(II) and cobalt(II) complexes, but with some small differences. The copper(II) complexes are probably therefore is isostructural with the nickel(II) and cobalt(II) complexes, but with the distortions usually found for copper(II).

Complexes with Deprotonated Medpco

We earlier determined[11] the X-ray structure of Cu_2(medpco-2H)Cl_2 which is shown in Figure 3. The deprotonated ligand has both coordination sites available and functions as a binucleating ligand. Each copper(II) is five-coordinate, being coordinated by a bridging *N*-oxide oxygen, a deprotonated

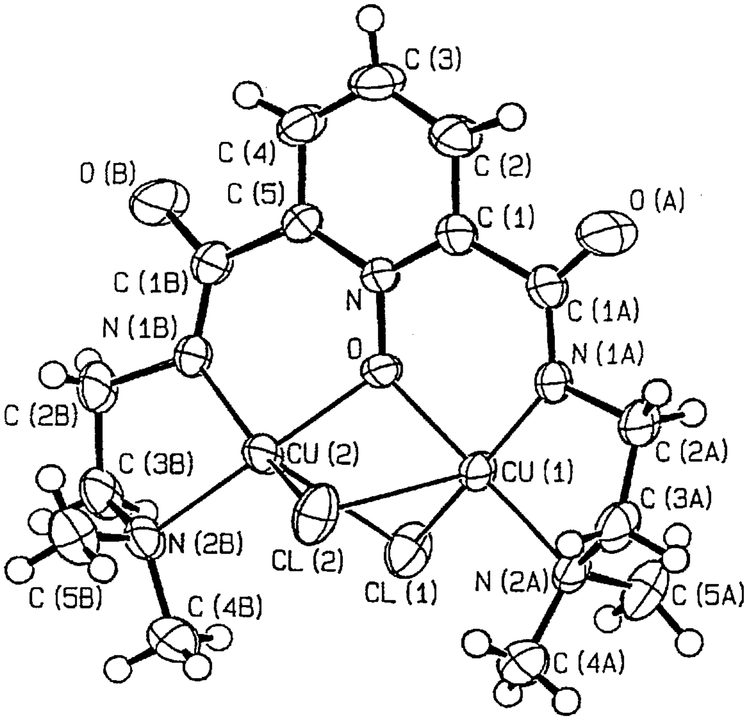


FIGURE 3 Structure of $Cu_2(medpco\text{-}2H)Cl_2$.

amide nitrogen, a tertiary amine nitrogen and two bridging chlorides. The reflectance electronic spectra of a series of copper(II) complexes of the type $Cu_2(medpco\text{-}2H)X_2$ were found to have a single absorption band in the range *ca.* 13000–16000 cm^{-1}, in keeping with the *N*-oxide-bridged structures in which the two copper(II) ions occupy similar coordination sites.[11]

The electronic spectra of the new nickel(II) and cobalt(II) complexes of the type $M_2(medpco\text{-}2H)Hal_2$ are very similar to those of the corresponding 1 : 1 complexes $M(medpco)Hal_2$ with neutral ligand. For reasons discussed with the 1 : 1 complexes, these spectra are characteristic of five-coordinate structures. Furthermore, the spectra indicate that the two metal ions in the $M_2(medpco\text{-}2H)Hal_2$ complexes are in similar environments. These observations support binucleated structures analogous to that found for $Cu_2(medpco\text{-}2H)Cl_2$.

The X-ray powder diffraction patterns of the $Ni_2(medpco\text{-}2H)Hal_2$ complexes are different and do not resemble the diffraction patterns of any other complexes. The X-ray powder diffraction patterns of the cobalt complexes, however, show that they are isostructural.

The magnetic properties of the Ni_2(medpco-2H)Hal_2 complexes, with small temperature variations, show little evidence for significant magnetic interaction. However, larger decreases in μ_{eff} with decreasing temperature, and more negative θ values, are found for the Co_2(medpco-2H)Hal_2 complexes. It is difficult to definitely equate this with antiferromagnetism, because of the temperature variations of μ_{eff} found for monomeric cobalt(II) complexes.[20] However, the room temperature μ_{eff} values for these Co_2(medpco-2H)Hal_2 complexes are 0.3–0.5 BM lower than for the apparently monomeric 1 : 1 Co(medpco)Hal_2 complexes. Furthermore, the temperature decreases of μ_{eff}, and the negative θ values, are larger for Co_2(medpco-2H)Hal_2 than for the Co(medpco)Hal_2 complexes. Since the coordination geometries for the cobalt(II) ions in Co_2(medpco-2H)Hal_2 are thought to be similar to those in the 1 : 1 Co(medpco)Hal_2 complexes, this is evidence for some antiferromagnetic interaction in the Co_2(medpco-2H)-Hal_2 complexes.

Supplementary Material

X-ray powder diffraction data are available on request.

References

[1] P. Zanello, S. Tamburini, P.A. Vigato and G.A. Mazzocchin, *Coord. Chem. Rev.*, **77**, 165 (1987).
[2] M.D. Glick and R.L. Lintvedt, *Prog. Inorg. Chem.*, **21**, 233 (1976).
[3] (a) M. Inoue and M. Kubo, *Coord. Chem. Rev.*, **21**, 1 (1976); (b) L. Rosenberg, L.K. Thompson, E.J. Gabe and F.L. Lee, *J. Chem. Soc., Dalton*, 625 (1986).
[4] B.M. Rapko, E.N. Duesler, P.H. Smith, R.T. Paine and R.R. Ryan, *Inorg. Chem.*, **32**, 2164 (1993).
[5] L.C. Nathan, C.A. Doyle, A.M. Mooring, D.C. Zapien, S.K. Larsen and C.G. Pierpont, *Inorg. Chem.*, **24**, 2763 (1985).
[6] G. Bombieri, S. Degetto, E. Forsellini and G. Marangoni, *Cryst. Struct. Commun.*, **6**, 115 (1977).
[7] E. Bullita, U. Casellato, P. Guerriero, P.A. Vigato and R. Graziani, *Inorg. Chim. Acta*, **134**, 3 (1987).
[8] S. Degetto, L. Baracco and M. Faggin, *J. Inorg. Nucl. Chem.*, **43**, 2413 (1981).
[9] A.B. Blake, E. Sinn, A. Yavari, B. Moubaraki and K.S. Murray, *Inorg. Chim. Acta*, **229**, 28 (1995).
[10] M. Antolovich, D.J. Phillips and A.D. Rae, *J. Chem. Soc., Chem. Commun.*, 582 (1984).
[11] M. Antolovich, D.J. Phillips and A.D. Rae, *Inorg. Chim. Acta*, **230**, 139 (1995).
[12] G.C. Chiumia, D.C. Craig, Imdadullah and D.J. Phillips, *Inorg. Chim. Acta*, **209**, 213 (1993).
[13] D.W. Smith, *Coord. Chem. Rev.*, **21**, 93 (1976).
[14] A.B.P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1984, Second Edition).

[15] B.D. Bird and P. Day, *J. Chem. Phys.*, **49**, 392 (1974).
[16] S.G.N. Roundhill, D.M. Roundhill, D.R. Bloomquist, C. Landee, R.D. Willett, D.M. Dooley and H.B. Gray, *Inorg. Chem.*, **18**, 831 (1979).
[17] M. Ciampolini, *Structure and Bonding*, **6**, 52 (1969).
[18] M. Ciampolini and G.P. Speroni, *Inorg. Chem.*, **5**, 45 (1966).
[19] F. Lions, I.G. Dance and J. Lewis, *J. Chem. Soc.* (*A*), 565 (1967).
[20] (a) B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1964); (b) A. Earnshaw, *Introduction to Magnetochemistry* (Academic Press, London, 1968); (c) L. Banci, A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *Struct. Bond.*, **52**, 37 (1982).