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Crystal Structure and Spectroscopic Properties of *N,N'*-bis(8-quinolilethylenediamine)monochlorocopper(II) Perchlorate

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Abstract

The crystal structure of the title compound, $[Cu(nn)Cl]ClO_4$, where nn = *N,N'*-bis(8-quinolilethylenediamine) has been determined by X-ray diffraction using diffractometer data collection. The Cu atom was located from a Patterson synthesis and the remaining non-hydrogen atoms were found from a subsequent Fourier synthesis. The new compound crystallises in the monoclinic space group $P2_1/n$ with $a = 15.647(3)$, $b = 9.775(2)$, $c = 14.156(3)$ Å, $\beta = 107.71(2)^\circ$ and $Z = 4$. The CuN_4Cl chromophore forms an intermediate geometry between a distorted tetragonal pyramid and a distorted bipyramid trigonal. The polycrystalline and frozen solution ESR spectra are reported between 77 K and room temperature. The molecular g tensor in the frozen solution is best consistent with the square pyramidal distorted stereochemistry in which an N atom occupies the axial position. The ESR spectrum does not change with the temperature. Extended Hückel calculations show the unpaired electron predominantly in the $d_{x^2-y^2}$ orbital, in accordance with the proposed geometry.

Introduction

In the literature data, structural and spectroscopic results in CuL_5 polyhedra where L = Cl, Br or a N or O donor atom are generally in accord with a square pyramidal stereochemistry which is elongated in the apical position [1]. A compressed trigonal bipyramid may eventually be stabilised if geometric ligand effects (polydentate ligands) and/or packing effects (bridging ligands) are present [1, 2]. These polydentate ligands are generally bidentate as 2,2-bipyridyl and similar, or tetradentate (tren). A fluxional behaviour may exist in these two geometries. In order to determine the influence of a tetradentate non-macrocyclic ligand on these geometries, the synthesis and crystal structure of $[Cu(nn)Cl]ClO_4$ (nn = *N,N'*-bis(8-quinolilethylenediamine)) has been determined, showing a distorted square pyramid geometry, which is confirmed by frozen solution ESR measurements and Extended Hückel calculations.

Experimental

Preparation

$[Cu(nn)Cl_2]$ previously reported by us [3] was dissolved in water. The solution was filtered and twice the stoichiometric quantity of $NaClO_4$ was added. A green precipitate appears immediately, which was filtered and recrystallized in acetonitrile. The green solution formed was filtered and left to evaporate in air. After 3–4 days, small and well formed green crystals were deposited. *Anal.* Found: C, 47.1; N, 10.7; H, 3.4; Cl, 13.8. Calc.: C, 46.84; N, 10.39; H, 3.51; Cl, 13.83%.

Crystal Data for [Cu(nn)Cl]ClO₄

$[C_{20}H_{18}N_4ClCu]ClO_4$, $M_r = 512.8$; monoclinic, $a = 15.647(3)$, $b = 9.775(2)$, $c = 14.156(3)$ Å, $\beta = 107.71(2)^\circ$, $V = 2062(1)$ Å^3, $P2_1/n$, $D_x = 1.651$ g cm^{-3}, $Z = 4$; $F(000) = 1044$; λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 13.96 cm^{-1}. Room temperature.

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determined from 15 reflections ($4 \leqslant \theta \leqslant 9^\circ$) and refined by least-squares. Intensities were collected with Mo Kα radiation, using the ω-scan technique (scan width 1° and scan speed 0.03° s^{-1}). Three reflections were measured every two hours as orientation and intensity control; significant variation was not observed. 2896 reflections were measured in the range $2 \leqslant \theta \leqslant 30^\circ$; 2827 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Lorentz-polarization, but no absorption, corrections were made.

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The Cu atom was located from a Patterson synthesis and the remaining non-hydrogen atoms from a subsequent Fourier synthesis. The structure was isotropically and anisotropically refined by full-matrix least-squares method, using the SHELX76 computer program [4]. The function minimized was $w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.0028|F_o|^2)^{-1}$, f, f' and f'' were taken from International Tables of X-Ray Crystallography [5]. The ΔF-synthesis computed after three isotropic refinements cycles gave five peaks around the chlorine atoms of the perchlorate ion assumed to be oxygen atoms. Thereby, we consider a disorder in the localization of oxygen atoms. 17 (of 18) H atoms were located in a difference synthesis and refined with an overall isotropic temperature factor, and anisotropically the remaining atoms. The final R value was 0.057 (R_w = 0.064) for all observed reflections. The positional parameters of non-hydrogen atoms are given in Table I.

TABLE I. Positional Parameters of Non-hydrogen Atoms ($\times 10^4$) with Estimated Standard Deviations in Parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu	46992(4)	11521(7)	12753(5)
Cl(1)	5956(1)	1733(2)	912(1)
N(1)	5416(3)	182(5)	2525(4)
C(2)	5968(5)	−828(8)	2543(6)
C(3)	8410(6)	3681(9)	1569(8)
C(4)	6635(6)	−722(9)	4296(7)
C(5)	6039(5)	378(8)	4316(5)
C(6)	5418(4)	783(7)	3393(5)
C(7)	4814(5)	1866(7)	3353(5)
C(8)	4859(6)	2520(9)	4233(6)
C(9)	5503(8)	2147(13)	5129(6)
C(10)	6051(6)	1070(10)	5165(6)
N(11)	4206(4)	2224(6)	2411(4)
C(12)	3271(5)	1662(9)	2216(6)
C(13)	3264(5)	140(8)	1992(5)
N(14)	3556(3)	−79(5)	1096(4)
C(15)	2896(4)	322(6)	177(5)
C(16)	3084(4)	1484(6)	−313(5)
N(17)	3890(3)	2107(5)	103(4)
C(18)	4085(5)	3227(7)	−334(5)
C(19)	3491(5)	3796(8)	−1190(6)
C(20)	2703(6)	3173(9)	−1613(6)
C(21)	2463(5)	1978(7)	−1199(5)
C(22)	1660(5)	1186(9)	−1608(6)
C(23)	1495(5)	61(8)	−1125(6)
C(24)	2093(5)	−371(8)	−241(6)
Cl(2)	6055(1)	3967(2)	−1917(1)
O(1)	5487(7)	4692(11)	−1562(9)
O(2)	6717(7)	3163(9)	8668(9)
O(3)	5518(10)	2871(10)	7660(12)
O(4)	6100(8)	4508(11)	7188(8)
O(5)	6764(10)	4998(14)	8415(16)

Results and Discussion

Crystal Structure

The crystal structure consists of two $Cu(nn)Cl^+$ cations and two ClO_4^- anions (Fig. 1). The structure of the cation (Fig. 2) involves a five-coordinate CuN_4Cl chromophore with an intermediate stereochemistry between a square pyramid and a trigonal bipyramid, with no evidence for even semi-coordination of the ClO_4^- anion or Cl ligand (of other cation). Effectively, the Cu·····O(1) distance and Cu·····Cl(1) distances are, respectively, 4.101 and 4.081 Å.

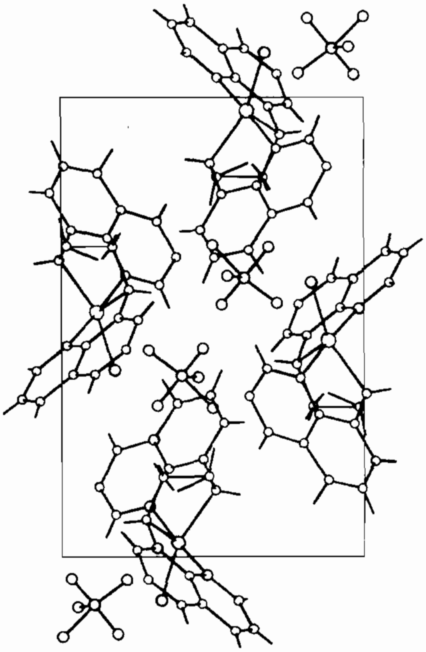

Fig. 1. Crystal structure of $[Cu(nn)Cl](ClO_4)$.

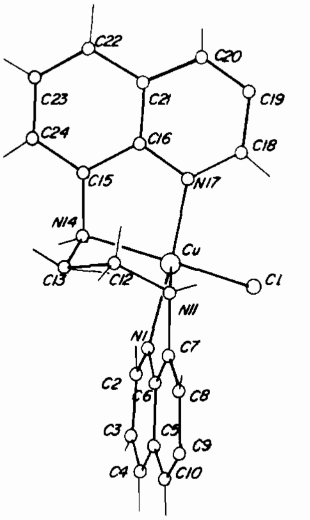

Fig. 2. Molecular structure of $[Cu(nn)Cl]^+$ cation with the atom-numbering scheme used.

TABLE II. Principal Bond Angles (°) with Estimated Standard Deviations in Parentheses

N(1)–Cu–Cl(1)	91.6(2)
N(11)–Cu–Cl(1)	124.1(2)
N(11)–Cu–N(1)	79.1(2)
N(14)–Cu–Cl(1)	152.3(2)
N(14)–Cu–N(1)	93.6(2)
N(14)–Cu–N(11)	83.6(2)
N(17)–Cu–Cl(1)	94.0(1)
N(17)–Cu–N(1)	174.2(2)
N(17)–Cu–N(11)	96.3(2)
N(17)–Cu–N(14)	82.3(2)
C(2)–N(1)–Cu	124.0(5)
C(6)–N(1)–Cu	115.9(4)
C(6)–N(1)–C(2)	119.2(6)
C(6)–C(5)–C(4)	117.3(7)
C(10)–C(5)–C(4)	123.5(8)
C(10)–C(5)–C(6)	119.2(8)
C(5)–C(6)–N(1)	121.4(6)
C(7)–C(6)–N(1)	118.1(5)
C(7)–C(6)–C(5)	120.5(6)
C(8)–C(7)–C(6)	117.5(7)
N(11)–C(7)–C(6)	118.1(5)
N(11)–C(7)–C(8)	124.4(7)
C(9)–C(8)–C(7)	121.2(9)
C(10)–C(9)–C(8)	120.7(8)
C(9)–C(10)–C(5)	120.7(8)
C(7)–N(11)–Cu	106.2(4)
C(12)–N(11)–Cu	103.0(4)
C(12)–N(11)–C(7)	114.5(5)
C(13)–C(12)–N(11)	109.9(6)
N(14)–C(13)–C(12)	109.4(6)
C(13)–N(14)–Cu	106.6(4)
C(15)–N(14)–Cu	107.6(4)
C(15)–N(14)–C(13)	114.0(5)
C(16)–C(15)–N(14)	117.5(5)
C(24)–C(15)–N(14)	123.8(6)
C(24)–C(15)–C(16)	118.7(6)
N(17)–C(16)–C(15)	116.9(5)
C(21)–C(16)–C(15)	121.4(6)
C(21)–C(16)–N(17)	121.7(6)
C(16)–N(17)–Cu	115.0(4)
C(18)–N(17)–Cu	126.4(4)
C(18)–N(17)–C(16)	118.5(5)
C(19)–C(18)–N(17)	122.7(6)
C(20)–C(19)–C(18)	119.0(7)
C(21)–C(20)–C(19)	121.1(7)
C(20)–C(21)–C(16)	116.9(6)
C(22)–C(21)–C(16)	116.9(7)
C(22)–C(21)–C(20)	126.1(7)
C(23)–C(22)–C(21)	120.6(7)
C(24)–C(23)–C(22)	121.5(7)
C(23)–C(24)–C(15)	120.8(7)

TABLE III. Principal Bond Lengths (Å) with Standard Deviations in Parentheses

Cl(1)–Cu	2.251(2)
N(1)–Cu	2.020(5)
N(11)–Cu	2.243(5)
N(14)–Cu	2.106(5)
N(17)–Cu	1.987(5)
C(2)–N(1)	1.307(8)
C(6)–N(1)	1.361(8)
C(5)–C(4)	1.429(12)
C(6)–C(5)	1.427(9)
C(10)–C(5)	1.375(11)
C(7)–C(6)	1.408(9)
C(8)–C(7)	1.383(9)
N(11)–C(7)	1.426(8)
C(9)–C(8)	1.407(14)
C(10)–C(9)	1.349(15)
C(12)–N(11)	1.508(9)
C(13)–C(12)	1.520(11)
N(14)–C(13)	1.490(8)
C(15)–N(14)	1.447(8)
C(16)–C(15)	1.409(8)
C(24)–C(15)	1.390(9)
N(17)–C(16)	1.363(7)
C(21)–C(16)	1.417(8)
C(18)–N(17)	1.338(8)
C(19)–C(18)	1.399(9)
C(20)–C(19)	1.341(11)
C(21)–C(20)	1.410(11)
C(22)–C(21)	1.438(10)
C(23)–C(22)	1.360(11)
C(24)–C(23)	1.382(11)
O(1)–Cl(2)	1.348(8)
O(2)–Cl(2)	1.358(8)
O(3)–Cl(2)	1.380(11)
O(4)–Cl(2)	1.394(9)
O(5)–Cl(2)	1.467(14)
O(5)–O(2)	1.836(17)
O(5)–O(4)	1.797(20)

The Cu, N(1), N(11) and N(17) atoms are nearly plane (largest deviation from the mean plane is –0.048(3) Å in Cu atom). This could correspond to the equatorial plane of bpt geometry, but the angles are very different from 120° (Table II): N(1)–Cu–N(11) = 79.1(2)°; N(1)–Cu–N(17) = 174.2(2)° and N(11)–Cu–N(17) = 96.3(2)°. On the other hand, the two possible apical positions, N(14) and Cl, are very deviated: the angle between N(14)–Cu–Cl is 152.3(2) instead of 180°. If we consider the possible square pyramid geometry, the Cu, Cl, N(1) and N(17) atoms are nearly in a plane (largest deviation from this plane is –0.06 Å in N(17) atom). In this case N(14) is very deviated (0.922 Å). With this hypothesis, N(11) atom occupies the apical position. The average distance of Cu–N(in plane) (Table III) is 2.037(6) Å, while the Cu–N(axial) distance is greater, 2.243 Å. This fact agrees with the distances given in the literature for $K[Cu(NH_3)_5][PF_6]_3$ [6] a nearly perfect square pyramid geometry: average Cu–N(in plane) distance equal to 2.102 Å and 2.193 Å for the Cu–N(axial) distance. This much larger apical bond compared to the equatorial bond length, which is reminiscent of the tetragonal elongation of octahedral Cu(II) complexes, is the consequence of the first-order Jahn–

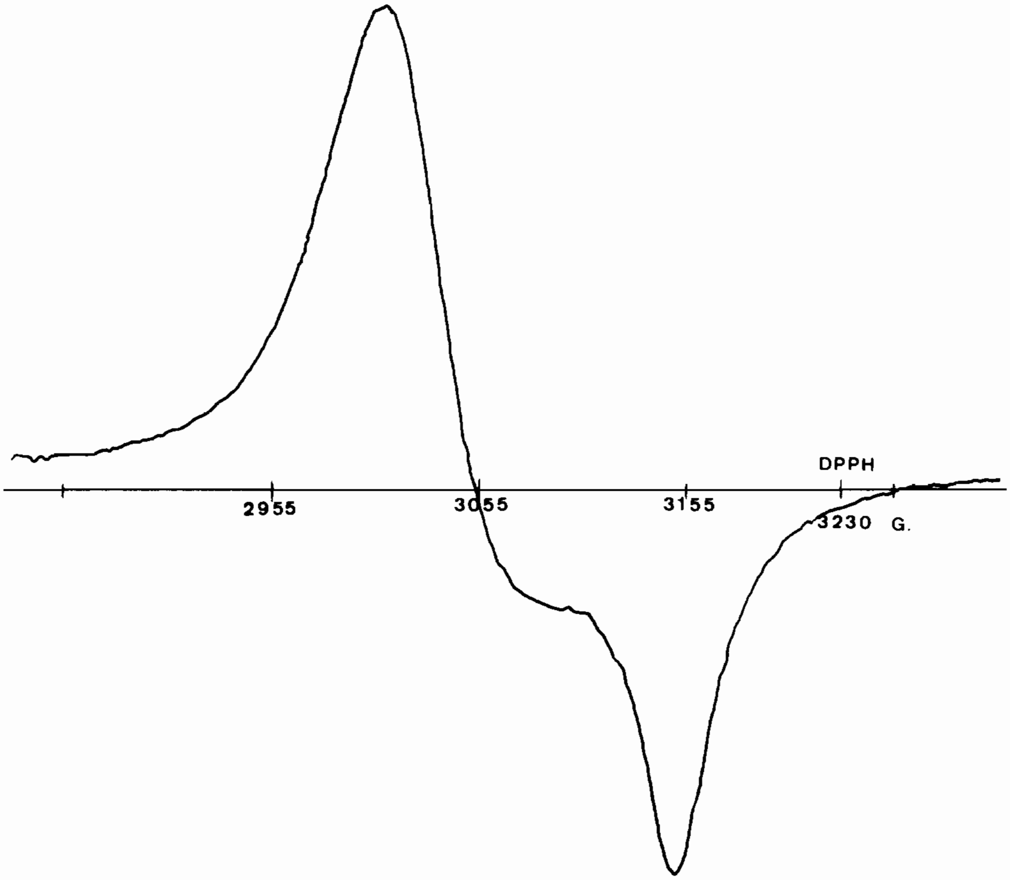

Fig. 3. Polycrystalline ESR spectrum of $[Cu(nn)Cl]ClO_4$ at 77 K or room temperature (microwave frequency = 8.922 GHz).

Teller effect [2, 7]. The distance Cu–Cl is 2.251 Å, greater than the Cu–N distances, which agrees with the literature data for $[Cu(bipy)Cl)]PF_6$ [1] and $[Cu(bipy)_2Cl]Cl{\cdot}6H_2O$ [8] (average Cu–N distance is 2.05 Å and Cu–Cl is 2.35 Å). Consequently all these structural data seem to indicate that the most approximate geometry to describe the new complex is the distorted square pyramid. This geometry has been adequately confirmed by spectroscopic measurements and Extended Hückel calculations, as indicated below. We can suppose that the distorted square pyramid geometry is due, in part, to the electronic and steric effects of the nn ligand, taking into account that in the other tetradentate ligand tren (tris-(2-aminoethyl)amine) and its derivatives the steric effects of the ligand forces the bpt geometry, with NH_3, Br or SCN in one axial position [6, 9, 10].

Electronic Spectra

The crystals of the title compound are green. The electronic reflectance spectra in the visible region is quite simple: it presents a shoulder near 10 000 cm^{-1} (1000 nm) and a broad, well defined maximum at 15 750 cm^{-1} (635 nm). These bands agree with the polarized single-crystal electronic spectrum of $K[Cu(NH_3)_5](PF_6)_3$ [11–13], which presents a square pyramid geometry [6]. The assignment, as previously suggested, is: the shoulder at near 10 000 cm^{-1} as $d_{z^2} \rightarrow d_{x^2-y^2}$ and the band maximum at 15 750 cm^{-1} as the $(d_{xz}, d_{yz}) \rightarrow d_{x^2-y^2}$ transitions [11–13]. If the complex would be best described as bpt geometry, it must present these two bands interchanged, that is to say, a band maximum near 11 000 cm^{-1} and a shoulder near 15 000 cm^{-1}, as has been described in the literature for many bpt analogues [6, 14–17].

ESR Measurements

The polycrystalline powder ESR spectrum (Fig. 3) shows $g_{\|} = 2.06$ and $g_{\perp} = 2.15$. These values are not in agreement with either of the two patterns expected for copper(II) pentacoordinate systems [18] $g_{\perp} > g_{\|} \simeq 2.00$ in bpt and $g_{\|} > g_{\perp}$ in sp. They would reflect crystal rather than molecular data. Indeed, frozen solution spectra in acetonitrile (Fig. 4), yields the usual pattern $g_{\|} = 2.28$, $A_{\|} = 160 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.06$, which shows that the unpaired electron is in a $x^2 - y^2$ orbital, as is described in the abovementioned $[Cu(NH_3)_5]^{2+}$ cation [6]. Therefore, the coordination can be best described as a distorted tetragonal pyramid, in which N(11) occupies the axial position.

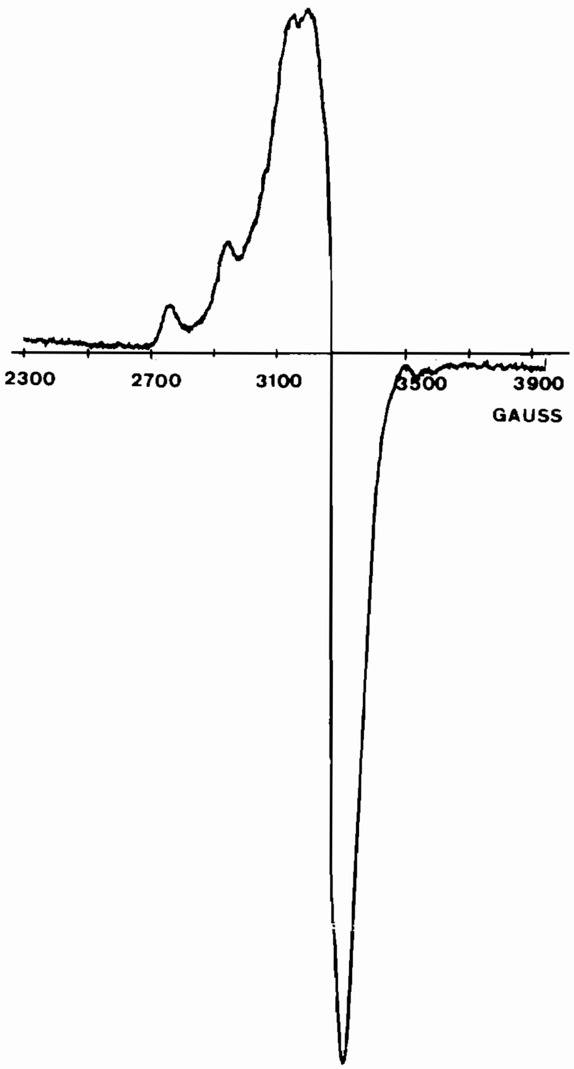

Fig. 4. Frozen solution ESR (in CH_3CN of $[Cu(nn)Cl]ClO_4$ at 77 K (microwave frequency = 9.483 GHz).

Extended Hückel Calculations

The Extended Hückel calculation has been carried out without iteration procedures, using the ICON 85 program. The calculation was carried out in the $[Cu(nn)Cl]^+$ cation using the crystallographic bond-length and angle data of the CuN_4Cl chromophore. In order to simplify the calculation, it has been also carried out with the hypothetical CuH_4Cl anion, supposing the same geometry. Both cases are equivalent. The HOMO is predominantly the atomic orbital $d_{x^2-y^2}$ (with a low contribution of the d_{z^2}). The order of the four following orbitals is: d_{xz} plus d_{z^2} (the former being predominant); d_{xy}, d_{z^2} and d_{xy} plus d_{yz}. The three last orbitals are very equal in energy. Consequently, the sequence of one-electron energy levels in the complex is comparable to that obtained in the equivalent crystal field calculation except that, due to the distortion of the chromophore, the d_{z^2} level is slightly stabilized and the d_{xz} destabilized, relatively to d_{xy} and d_{yz} atomic orbitals.

The atomic net charge is greater for the N(11) atom (apical position). The atomic orbital occupation is almost of two electrons (1.99) for d_{z^2}, d_{xy}, d_{xz} and d_{yz} and lower (1.4) for $d_{x^2-y^2}$ indicating, once again, that the unpaired electron is in this orbital.

Supplementary Material

Structure factors, thermal parameters and H atom coordinates are available from the authors on request.

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References

1 S. Tyaji, B. Hathaway, S. Kremer, H. Stratemeir and D. Reinen, *J. Chem. Soc., Dalton Trans.*, 2087 (1984) and refs. therein.
2 D. Reinen and C. Friedel, *Inorg. Chem., 23,* 791 (1983).
3 J. Casabó, J. Ribas, C. Diaz and J. Vilana, *An. Quím., 81,* 178 (1985).
4 G. M. Sheldrick, 'SHELX 1976', a computer program for crystal structure determination, University of Cambridge, 1976.
5 'International Tables of X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
6 M. Duggan, N. Ray and B. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1342 (1980).
7 D. Reiner and C. Friedel, *Struct. Bonding (Berlin), 37,* 1 (1979).
8 S. Tyaji, B. Hathaway, S. Kramer, H. Stratemeir and D. Reinen, *J. Chem. Soc., Dalton Trans.*, 2087 (1984).
9 P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc., 89,* 6131 (1967).
10 M. D. Vaira and P. L. Oriol, *Acta Crystallogr., Sect. B, 24,* 595 (1968).
11 J. S. Wood, *Prog. Inorg. Chem., 16,* 227 (1972).
12 B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev., 5,* 1 (1970).
13 B. J. Hathaway and A. A. G. Tomlinson, *J. Chem. Soc. A,* 1905 (1968).
14 B. J. Hathaway and D. E. Dilling, *Coord. Chem. Rev., 5,* 143 (1970).
15 A. R. Rossi and R. Hoffman, *Inorg. Chem., 14,* 365 (1975).
16 M. Ciampolini and N. Nardi, *Inorg. Chem., 5,* 1150 (1966).
17 J. S. Wood, *Inorg. Chem., 7,* 852 (1968).
18 A. Bencini, I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem., 17,* 3194 (1978) and refs. therein.