X-ray, Spectroscopic and Magnetic Studies of Hexaaquacopper(II) Di(diphenylphosphate) Diglycine

TADEUSZ GŁOWIAK* and IRENA PODGÓRSKA

Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

(Received February 12, 1986; revised June 9, 1986)

Abstract

A new copper(II) complex, $[Cu(H_2O)_6] \cdot 2DPhP \cdot 2Gly$ ($DPhP = (C_6H_5O)_2PO_2^-$, diphenylphosphate monoanion; $Gly = {}^-O_2C-CH_2-NH_3^+$) was prepared and characterized by means of crystallographic, spectroscopic and magnetic measurements.

Crystals of the title compound are triclinic, space group $P\bar{1}$, with $a = 17.019(6)$, $b = 6.520(3)$, $c = 8.107(3)$ Å, $\alpha = 93.39(5)$, $\beta = 89.20(5)$, $\gamma = 94.86(5)°$ and $Z = 1$. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares method to $R = 0.038$ for 3329 independent reflections with $I > 1.96 \sigma(I)$.

The structure of the title compound contains discrete centrosymmetric $[Cu(H_2O)_6]^{2+}$ cations with a tetragonally distorted octahedral coordination geometry about the copper ions, uncoordinated glycine zwitterionic molecules and diphenylphosphate monoanions.

Introduction

In the course of research into mixed-ligand complexes of copper(II) with aromatic phosphate ligands, we have attempted to prepare complexes in which amino acid molecules are also present [1]. The study of the molecular structure of copper(II) complexes of amino acids and their derivatives has been of interest in the field of bioinorganic chemistry [2, 3]. In particular, the identification and determination of the nature of the binding sites of amino acid molecules has been the dominant subject of many current investigations. Because of the chemical specificity of Cu(II) ions, they are able to bind to several positions on these ligands, giving rise to quite different coordination modes of the ligands [4–7]. It is extremely interesting in the case of mixed-ligand complexes of copper(II) where amino acid molecules are present. In this paper we report the results of the crystal structure determinantion

as well as spectral and magnetic investigations of a second such complex, namely $[Cu(H_2O)_6] \cdot 2DPhP \cdot 2Gly$.

Experimental

The compound of formula $[Cu(H_2O)_6] \cdot 2DPhP \cdot 2Gly$ was obtained by dissolving the $[Cu(DPhP)_2(H_2O)_2]$ complex [8] in water containing an excess of glycine. By allowing the resultant solution to stand for several days at room temperature (about 295 K), light-blue crystals appeared. The compound was repeatedly recrystallized in water to obtain suitable crystals for X-ray analysis. *Anal.* Calc. for $C_{28}H_{42}CuN_2O_{18}P_2$: C, 41.00; H, 5.17; N, 3.42. Found: C, 41.08; H, 5.23; N, 3.38%.

The diffuse reflectance spectrum of the undiluted powder sample was measured at room temperature in the range 350–2000 nm with a Beckman UV 5240 spectrophotometer.

The room-temperature magnetic moment was measured with the Gouy method, using $HgCo(SCN)_4$ as a susceptibility standard and correcting for diamagnetism with the appropriate Pascal constants [9, 10].

The EPR spectra both of the polycrystalline sample (at room-temperature) and the DMSO frozen-solution were measured on a JEOL JES-ME-3X spectrometer equipped with MJ-110 R magnetic-field marker, in the X-band, at $\nu = 9.25$ GHz.

The crystal selected for X-ray analysis was mounted on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and graphite monochromator. Accurate unit-cell dimensions (the diffraction group and the approximate cell dimensions being determined from rotation and Weissenberg photographs) were obtained by least-squares refinement of the observed setting angles for 15 high-order independent reflections measured with Mo Kα radiation.

A total 3389 reflections were measured under conditions listed in Table I, and were corrected for Lorentz polarization effects, but not for absorption

---

*Author to whom correspondence should be addressed.

TABLE I. Summary of Crystal Data Collection

Diffractometer	Syntex $P2_1$
Radiation	Mo Kα
T (K)	295
Space group	$P\bar{1}$
a (Å)	17.019(6)
b (Å)	6.520(3)
c (Å)	8.107(3)
α (°)	93.39(5)
β (°)	89.20(5)
γ (°)	94.86(5)
V (Å^3)	894.7
Molecular formula	$C_{28}H_{42}CuN_2O_{18}P_2$
Molecular weight	820.2
Z	1
$F(000)$	427
D_c (Mg m^{-3})	1.52
D_o (Mg m^{-3})	1.52(1) (by flotation)
Scan mode	$\theta/2\theta$
Scan range (2θ)	2.0 to 60.5°
Scan rate	2.0 to 29.3° min^{-1}
Reflections collected	3389
Reflections observed	3329 with $I > 1.96 \, \sigma(I)$
R	0.038
R_w	0.047
Parameters	232
Crystal size (mm)	0.15 × 0.4 × 0.25
Absorption coefficient (cm^{-1})	8.1

Fig. 1. A perspective view of the $[Cu(H_2O)_6]^{2+}$ ion with the atom numbering scheme.

in view of the small crystal dimensions and low absorption coefficient. Two selected reflections were monitored every 100 intensities. No significant variation in their intensities occurred during the data collection. The structure determination was based on the 3329 reflections with $I > 1.96 \, \sigma(I)$.

Determination and Refinement of the Structure

The centrosymmetric space group $P\bar{1}$ was initially assumed and then confirmed by the subsequent refinement of the structure, which was determined by the heavy-atom and Fourier techniques. Isotropic full-matrix least-squares refinement of all non-hydrogen atoms yielded $R = 0.092$. Introduction of anisotropic thermal parameters for all 26 non-hydrogen atoms gave an R value of 0.052. 11 hydrogen atoms (these from glycine and water molecules) were found from the difference Fourier map, while the positions of the remaining hydrogen atoms (from phenyl rings) were calculated using the HPSON program. All 21 hydrogen atoms, with fixed positional and thermal parameters (B_{iso} = 4.5 Å^2), were added to the model structure but not refined.

Further full-matrix least-squares anisotropic refinement of non-hydrogen atoms led to final R, R_w and S values of 0.038, 0.047 and 3.673, respectively. For the final cycle of refinement, all parameter changes for non-hydrogen atoms were within 0.04
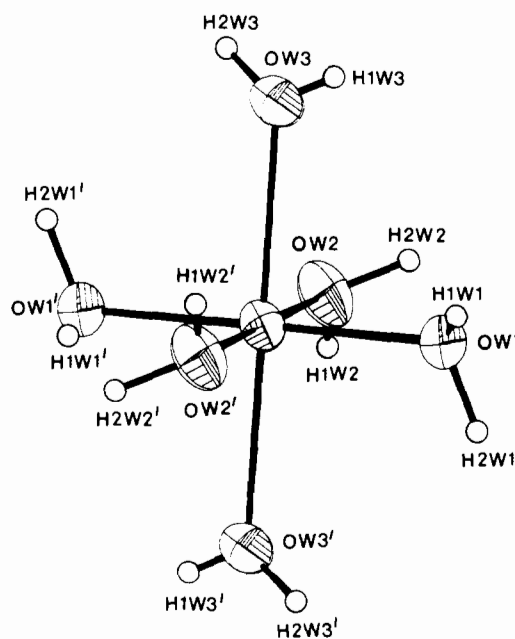
of their standard deviations. A final difference map showed no peaks higher than 0.30 e Å^{-3}.

Neutral-atomic scattering factors, including anomalous dispersion corrections for Cu and P atoms, were taken from the International Tables for X-ray Cystallography [11]. All calculations were performed on a Nova 1200 minicomputer by using the Syntex (1976) XTL/XTL-E Structure Determination System [12]. The perspective view of the complex molecule (Fig. 1) was obtained using the ORTEP II plotting program [13].

Final positional and thermal parameters for non-hydrogen atoms are given in Table II, while the bond distances and angles are listed in Table III. The geometry of the hydrogen bonds is given in Table IV.

Results and Discussion

The crystal structure of the title compound projected down the b axis is shown in Fig. 2, while Fig. 1 shows a perspective view of the hexaaqua-copper(II) cation with the atom numbering scheme used.

Description of the Structure

The most remarkable feature of this crystal structure is that the diphenylphosphate and glycine molecules are not coordinated to the copper, but are hydrogen-bonded to the water molecules that form the copper(II) ion coordination sphere.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and B_{eq} (Å^2) Values for Non-hydrogen Atoms with their Standard Deviations in Parentheses. $B_{eq} = 1/3\Sigma_i B_{ii}$

Atom	x	y	z	B_{eq}
Cu	0	0	0	2.17(3)
P	2441(1)	751(1)	2075(1)	2.44(5)
OW(1)	−932(1)	1430(3)	728(3)	3.25(17)
OW(2)	658(1)	2669(3)	106(2)	2.54(14)
OW(3)	301(1)	−305(3)	2753(2)	2.93(16)
O(1)	2041(1)	2558(3)	1602(3)	2.85(15)
O(2)	2091(1)	−1347(3)	1561(3)	2.84(15)
O(3)	2524(1)	765(3)	4049(3)	3.18(16)
O(4)	3329(1)	1119(3)	1417(3)	3.01(16)
O(5)	632(1)	4984(3)	−2521(2)	2.85(15)
O(6)	628(1)	2859(3)	−4763(3)	3.05(16)
N	1236(2)	5758(4)	−6741(3)	2.58(17)
C(11)	2745(2)	2523(5)	5043(4)	2.99(23)
C(12)	2543(2)	2464(6)	6702(4)	3.78(27)
C(13)	2741(2)	4160(7)	7741(4)	4.65(33)
C(14)	3135(2)	5911(6)	7156(5)	4.53(32)
C(15)	3340(2)	5947(6)	5521(5)	4.07(29)
C(16)	3146(2)	4244(5)	4445(4)	3.51(26)
C(21)	3912(2)	−219(5)	1722(4)	2.85(22)
C(22)	3826(2)	−2265(5)	1224(4)	3.44(25)
C(23)	4432(2)	−3485(6)	1458(5)	4.51(32)
C(24)	5112(3)	−2663(7)	2206(6)	5.89(42)
C(25)	5188(3)	−621(8)	2724(7)	6.50(47)
C(26)	4585(2)	623(6)	2493(6)	5.14(36)
C(1)	796(2)	4552(4)	−4015(3)	2.18(19)
C(2)	1226(2)	6251(4)	−4945(4)	2.44(20)

The copper(II) ions occupying the inversion centers have tetragonally rather than rhombically distorted octahedral coordination geometry. The $Cu-OH_2$ distances of 1.973(2), 1.986(2) and 2.321-(2) Å (tetragonality $T = 0.853$) differ somewhat from those observed for other compounds containing $[Cu(H_2O)_6]^{2+}$ ions [14–19]. As was shown earlier, the hexaaquacuprate ions exhibit a variety of structures, ranging from that of a highly elongated tetragonal geometry (practically square planar) in copper hydrogen maleate hydrate [19] with tetragonality of 0.726, through the rhombically distorted ions with three quite different bond lengths in the Tutton salts [14–17] with tetragonalities in the range 0.858–0.914, to the regular octahedral ion (though with a dynamic distortion) observed in the structure of $[Cu(SiF_6)] \cdot 6H_2O$ [18] with tetragonality of 1.000. It was also generally recognized that factors such as the size and bonding capacities of the present counterions and intermolecular hydrogen bonding tend to have a dominant influence on the geometry of complexes of this kind.

Comparing all available structural data we can note that the geometry of the hexaaquacopper(II) ion in our compound is very similar to those found for tallium and caesium Tutton salts [14, 17] and to that found in the crystal structure of $K_2[Cu(H_2O)_6](ZrF_6)_2$ compound [14]. According to the fluxional model [20] involving a potential energy surface of three possible elongated tetragonal octa-

TABLE III. Interatomic Distances (Å) and Angles (°) with the Standard Deviations in Parentheses

Hexaaquacopper(II) cation

Cu−OW(1)	1.973(2)		
Cu−OW(2)	1.986(2)		
Cu−OW(3)	2.321(2)		
OW(1)−Cu−OW(2)	90.2(1)	OW(1)−Cu−OW(2)	89.8(1)
OW(1)−Cu−OW(3)	88.9(1)	OW(1)−Cu−OW(3)	91.1(1)
OW(2)−Cu−OW(3)	87.9(1)	OW(2)−Cu−OW(3)	92.1(1)

Diphenyl phosphate monoanion

P−O(1)	1.481(2)	P−O(2)	1.483(2)
P−O(3)	1.608(2)	P−O(4)	1.600(2)
O(3)−C(11)	1.390(4)	O(4)−C(21)	1.409(4)
C(11)−C(12)	1.385(5)	C(21)−C(22)	1.367(5)
C(12)−C(13)	1.372(6)	C(22)−C(23)	1.377(5)
C(13)−C(14)	1.379(6)	C(23)−C(24)	1.368(6)
C(14)−C(15)	1.366(5)	C(24)−C(25)	1.368(7)
C(15)−C(16)	1.391(5)	C(25)−C(26)	1.384(6)
C(16)−C(11)	1.373(5)	C(26)−C(21)	1.369(5)
O(1)−P−O(2)	118.9(1)	O(2)−P−O(3)	105.3(1)
O(1)−P−O(3)	110.7(1)	O(2)−P−O(4)	111.2(1)
O(1)−P−O(4)	105.6(1)	O(3)−P−O(4)	104.2(1)
P−O(3)−C(11)	123.7(2)	P−O(4)−C(21)	122.7(2)
O(3)−C(11)−C(12)	116.5(3)	O(4)−C(21)−C(22)	121.7(3)
C(11)−C(12)−C(13)	119.1(3)	C(21)−C(22)−C(23)	119.6(3)

(continued)

TABLE III *(continued)*

C(12)–C(13)–C(14)	121.0(4)	C(22)–C(23)–C(24)	120.3(4)
C(13)–C(14)–C(15)	119.5(4)	C(23)–C(24)–C(25)	119.7(4)
C(14)–C(15)–C(16)	120.5(4)	C(24)–C(25)–C(26)	120.6(5)
C(15)–C(16)–C(11)	119.2(3)	C(25)–C(26)–C(21)	118.9(4)
C(16)–C(11)–C(12)	120.7(3)	C(26)–C(21)–C(22)	120.9(3)
C(16)–C(11)–O(3)	122.8(3)	C(26)–C(21)–O(4)	117.4(3)

Glycine molecule

O(5)–C(1)	1.260(3)	C(1)–C(2)	1.509(4)
O(6)–C(1)	1.241(3)	C(2)–N	1.473(4)
O(5)–C(1)–O(6)	125.1(3)	O(6)–C(1)–C(2)	118.5(2)
O(5)–C(1)–C(2)	116.5(2)	C(1)–C(2)–N	112.2(2)

TABLE IV. The Hydrogen Bonds

Distances (Å)				Angle (°) DHA
D–H•••A	D–H	H•••A	D–A	
OW(1)–H(1)W(1)•••O(2)[i]	0.96	1.77	2.722(3)	170
OW(1)–H(2)W(1)•••O(5)[ii]	0.92	1.78	2.694(3)	171
OW(2)–H(1)W(2)•••O(5)	0.93	1.76	2.685(3)	166
OW(2)–H(2)W(2)•••O(1)	0.96	1.73	2.672(3)	171
OW(3)–H(1)W(3)•••O(6)[iii]	0.90	1.97	2.823(3)	158
OW(3)–H(2)W(3)•••O(6)[i]	0.88	1.92	2.781(3)	167
N–H(1)N•••O(2)[iv]	0.91	1.81	2.713(3)	171
N–H(2)N•••O(1)[v]	0.88	2.02	2.852(3)	157

Symmetry code: none (x, y, z); (i) $-x, -y, -z$; (ii) $-x, -y + 1, -z$; (iii) $x, y, z + 1$; (iv) $x, y + 1, z - 1$; (v) $x, y, z - 1$.
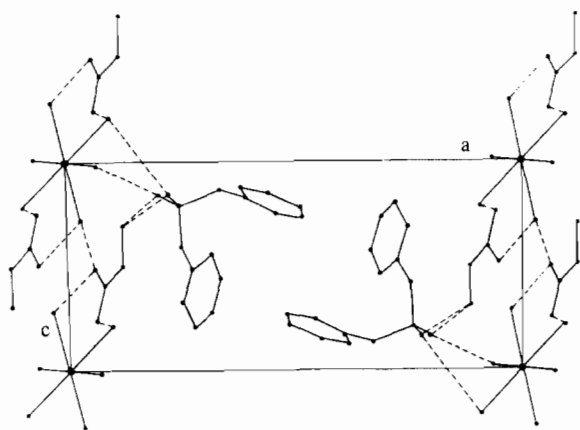

Fig. 2. The structure projected along b with the hydrogen-bonding scheme.

hedral CuO_6 chromophores, in the room-temperature structure of the caesium Tutton salt only the lowest potential well (I) is occupied, while the intermediate (II) and the highest (III) potential wells are unoccupied. The result is a non-temperature-variable elongated rhombic octahedral stereochemistry with a relatively low tetragonality, $T = 0.858$. In contrast to this, in the potassium and especially the ammonium Tutton salt there is great thermal population of well II at room temperature, and the tetragonalities increase to 0.881 and 0.914, respectively. After lowering of the temperature, an apparent elongation of the CuO_6 chromophore is observed, as well as a corresponding decrease in the observed tetragonalities, e.g. from 0.914 to 0.874 at 123 K for the ammonium salt [21]. At the lower temperature of 5 K [22], there is a further decrease in tetragonality to 0.860, which is very close in value to that of 0.858 observed in the caesium and tallium Tutton salts at room temperature. So it has been suggested that the room temperature crystal structure of the caesium salt is a fair representation of the underlying static stereochemistry of the ammonium Tutton salt [21].

The hexaaquacuprate(II) ions, diphenylphosphate monoanions and glycine zwitterionic molecules are connected by a network of hydrogen bonds. Each water molecule forms two hydrogen bonds with the oxygen atoms from both the glycine and diphenylphosphate moieties. Water molecule W(1) gives two nearly linear hydrogen bonds, $OW(1)•••O(2)^i$ (i:

$-x$, $-y$, $-z$) and $OW(1) \cdots O(5)^{ii}$ (ii: $-x$, $-y + 1$, $-z$), with the lengths and angles at hydrogen atoms of 2.722(3) Å, 170° and 2.694(3) Å, 171°, respectively. Water molecule W(2) has two relatively strong hydrogen bonding contacts: $OW(2) \cdots O(5)$ to the oxygen atom from the carboxylate group of glycine molecule, and $OW(2) \cdots O(1)$ to the oxygen atom of the diphenylphosphate ligand molecule. The corresponding lengths and angles are 2.685(3) Å, 166° and 2.672(3) Å, 171°, respectively. The third water molecule W(3) forms hydrogen bonds with oxygen atoms from two different glycine molecules. The first one, $OW(3) \cdots O(6)^{iii}$ (iii: x, y, $z + 1$), has a length of 2.823(3) Å and an angle at hydrogen atom of 158°; the second one, $OW(3) \cdots O(6)^{i}$, has a length of 2.781(3) Å and an angle at hydrogen atom of 167°.

The glycine molecule present in this structure in the zwitterionic form acts as both a donor and an acceptor of hydrogen bonds. Both oxygen atoms of the carboxylate group are involved in two such contacts of significantly different strength. That is why the C–O(5) and C–O(6) bond distances differ by $\sim$0.02 Å. The protonated amino group is a donor of two hydrogen bonds. Their lengths (to the oxygen atoms from two different diphenylphosphate molecules) are 2.713(3) and 2.852(3) Å, respectively.

The glycine molecule is planar except for the nitrogen atom, which deviates by $\sim$0.29 Å from the least-squares plane defined by the O(5), O(6), C(1) and C(2) atoms. Its conformation is given by the two angles ψ_1 and ψ_2, describing the torsion of the two C–O bonds about the single carbon–carboxylate–carbon(α) bond. The corresponding values of these angles are 12.2(4) and $-167.5(3)$°, respectively.

Important conformational parameters of the diphenylphosphate molecule are the torsion angles about both of the P–O(C) ester bonds. These two angles, ω and ω', are ±59.3(6) and ±70.4(5)°, respectively; so in the present compound the diester ion conformation with respect to the phosphate group is *gauche, gauche*. It is worth noting that exactly the same conformation of the diphenylphosphate monoanion has been found in the structure of glycinium diphenylphosphate [23], where the values of the corresponding angles were found to be ±61.4(4) and ±71.9(4)°, respectively. In contrast, in the crystal structures of two mixed-ligand copper(II) complexes with diphenylphosphate ligand, we have observed that the diester ligand co-ordinated to the metal ion is present in the *gauche, trans* conformation [1, 24]. The corresponding angles are $-179.8(2)$ and 77.0(2)° for ω and ω' in [Cu-(DPhP)$_2$(ImH)$_4$] [24] and 176.3(5), and $-72.8(6)$° for ω and ω' in [Cu$_2(\beta$-Ala)$_4$(DPhP)$_2$]·2DPhP·2H$_2$O [1], respectively. Thus, drastic conformational changes occur in the diphenylphosphate monoanion after coordination to the metal ion.

Spectroscopic and Magnetic Results

· The diffuse electronic reflectance spectrum of the powder sample contains a broad peak centered at 12 900 cm^{-1} and well defined shoulder at 10 000 cm^{-1} as well as other peaks occurring below 10 000 cm^{-1}, *i.e.*, at 7270, 6790 and 6010 cm^{-1}. The last two are assignable to infrared overtones of water molecules. This spectral feature is in good agreement with the distorted octahedral geometry for the title compound.

It is known that in most copper(II) compounds having distorted octahedral structures the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ lies closely in energy to the other 'd–d' transitions, *i.e.*, at $\sim$10 000–14 000 cm^{-1}; it has been assigned with this range in a number of copper(II) complexes containing [Cu(H$_2$O)$_6$]$^{2+}$ ions [25, 26]. But recently Hitchman and Waite have shown that these assignments of the spectra of some Tutton salts are wrong [27]. They have pointed out that the spectra of the deuterated analogues of compounds Cat$_2$Cu(SO$_4$)$_2$·6H$_2$O (where Cat = K$^+$, Rb$^+$, Tl$^+$, NH$_4^+$) and K$_2$Cu(ZrF$_6$)·6H$_2$O strongly suggest that in these salts the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ occurs at much lower energy (in the range 6000–8000 cm^{-1}). In their opinion this abnormally low energy in this class of compounds is probably due to the unusually short Cu–OH$_2$ bonds in the axial position.

The room-temperature polycrystalline and frozen-solution (DMSO, at 173 K) EPR spectra of the title compound exhibit parallel and perpendicular features typical of a Cu(II) ion in an axial ligand field with tetragonal distortion by elongation along the axial direction. For a Cu(II) ion in such a distorted octahedral geometry, two sets of lines are expected, centered at $g_\|$ and $g_\perp$. In the frozen-solution spectrum this effect is observed at $g_\|$ where three of the four lines are resolved, the fourth being obscured by the absorption around $g_\perp$. The four hyperfine lines at $g_\perp$ are not resolved since $A_\perp$ is usually much smaller than $A_\|$ in Cu(II) complexes [28]. The values of corresponding parameters are: $g_\| = 2.309$, $g_\perp = 2.065$ and $A_\| = 150$ Gs. For comparison, 'g' values obtained from polycrystalline EPR spectrum are $g_\| = 2.405$ and $g_\perp = 2.100$, respectively.

The room-temperature magnetic moment of 1.98 BM is consistent with the monomeric structure of the title compound.

Acknowledgements

References

1 T. Głowiak, I. Podgórska and J. Baranowski, *Inorg. Chim. Acta, 115*, 1 (1986).

2 A. H. Herlinger and T. V. Long, *J. Am. Chem. Soc., 92*, 6481 (1970).

3 L. Antolini, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 22*, 141 (1983) and refs. therein.

4 M. E. Kamwaya, E. Papavinasam and S. G. Teoh, *Acta Crystallogr., Sect. C, 40*, 2043 (1984).

5 L. Antolini, L. Menabue, G. C. Pellacani, G. Battistuzzi Gavidi, G. Grandi, L. P. Battaglia, A. Bonamartini Corradi and G. Marcotrigiano, *J. Chem. Soc., Dalton Trans.*, 1687 (1984).

6 Y. Sasada, A. Takenaka and T. Furuya, *Bull. Chem. Soc. Jpn., 56*, 1745 (1983).

7 L. P. Battaglia and A. Bonamartini Corradi, *Acta Crystallogr., Sect. B, 33*, 3896 (1977).

8 T. Głowiak and A. W. Szemik, in press.

9 A. Earnshow, 'Introduction to Magnetochemistry', Academic Press, London, 1968.

10 E. Konig, 'Magnetic Properties of Coordination and Organometallic Transition Metal Compounds', Springer-Verlag, Berlin, 1966.

11 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974.

12 'Syntex (1976)', XTL/XTLE Structure Determination System, Syntex Analytical Instruments, Cupertino, Calif., 1976.

13 C. K. Johnson, 'ORTEP II', Report ORNL-5138, Oak Ridge National Laboratory, Tenn., 1976.

14 G. M. Brown and R. Chibambaram, *Acta Crystallogr., Sect. B, 25*, 676 (1969).

15 D. J. Robinson and C. H. L. Kennard, *Cryst. Struct. Commun., 1*, 185 (1972).

16 J. J. Van der Zee, K. G. Shields, A. J. Graham and C. H. L. Kennard, *Cryst. Struct. Commun., 1*, 367 (1972).

17 K. G. Shields and C. H. L. Kennard, *Cryst. Struct. Commun., 1*, 189 (1972).

18 S. Ray, A. Zalkin and D. H. Templeton, *Acta Crystallogr., Sect. B, 29*, 2748 (1973).

19 C. K. Prout, J. R. Carruthers and F. J. C. Rossotti, *J. Chem. Soc. A*, 3342 (1971).

20 B. J. Hathaway, M. Duggan, A. Murphy, J. Mullane, C. Power, A. Walsh and B. Walsh, *Coord. Chem. Rev., 36*, 276 (1981).

21 N. W. Alcock, M. Duggan, A. Murray, S. Tyagi, B. J. Hathaway and A. Hewat, *J. Chem. Soc., Dalton Trans.*, 7 (1984).

22 G. Smith, F. H. Moore and C. H. L. Kennard, *Cryst. Struct. Commun., 4*, 407 (1975).

23 T. Głowiak and I. Wnęk, *J. Cryst. Spectrosc. Res., 15*, 157 (1985).

24 T. Głowiak and I. Wnęk, *Acta Crystallogr., Sect. C, 41*, 507 (1985).

25 R. A. Palmer, C. G. Roy and R. C. Roy, *J. Chem. Soc. A*, 3084 (1970).

26 K. Dawson, M. A. Hitchman, C. K. Prout and F. J. C. Rossotti, *J. Chem. Soc., Dalton Trans.*, 1509 (1972).

27 M. A. Hitchman and T. D. Waite, *Inorg. Chem., 15*, 2150 (1976).

28 G. F. Bryce, *J. Phys. Chem., 70*, 3549 (1966).