Benzotriazole Complexes. I. The Crystal Structure of Di-μ-chloro-bis[bis(benzotriazole)chlorocopper(II)] Monohydrate

INGER SØTOFTE and KURT NIELSEN

Structural Chemistry Group, Chemistry Department B, DTH 301, The Technical University of Denmark, DK-2800 Lyngby, Denmark

The crystal structure of the title compound, [Cu(C$_6$H$_5$N$_3$)$_2$Cl$_2$]$_2$·H$_2$O, has been investigated by X-ray diffraction techniques. The crystals are triclinic, space group $P\bar{1}$, with $a = 8.591(3)$ Å, $b = 11.906(4)$, $c = 16.083(4)$ Å, $\alpha = 110.62(5)°$, $\beta = 91.95(5)°$ and $\gamma = 92.04(6)°$. The structure was refined to $R = 0.053$. The complex consists of pairs of trigonal-bipyramidal copper(II) centers, which share an edge formed by two bridging chloride ions, each being equatorial. The equatorial coordination sites of copper are occupied by three chloride ligands, while the axial sites are occupied by two nitrogen atoms from two different benzotriazole groups. However, the coordination around one of the Cu-atoms can also be described as square pyramidal. The Cu—Cu separations in the two centrosymmetric, crystallographically independent dimers are 3.520(2) and 3.448(3) Å, the bridging Cu—Cl distances are 2.299(3), 2.694(4) and 2.441(4), 2.544(4) Å, respectively. The coordination to copper has only a small effect on the geometry of the benzotriazole groups. The packing of the structure may be described by layers consisting of Cu- and Cl-atoms separated by layers of almost parallel benzotriazole ligands.

Benzotriazole (abbreviated BTAH) is frequently used for corrosion inhibition on copper and its alloys, but so far only amorphous or microcrystalline compounds of copper with BTAH have been reported.[1] Furthermore, only a few organometallic compounds of BTAH have been examined by X-ray crystallographic methods.[2,3] Therefore, investigations of transition metal complexes with BTAH[4,5] are carried out and the present structure analysis is part of this work.

EXPERIMENTAL

Green crystals of the compound were precipitated by mixing 2×10^{-4} mol cupric chloride dihydrate in 2 ml of 2 M hydrochloric acid and 3×10^{-3} mol benzotriazole in 6−8 ml acetonitrile. The possible space groups were established from Weissenberg photographs using Cu-radiation. Unit cell dimensions and their standard deviations were determined by least-squares refinement based on reflections measured on a four-circle diffractometer. For data collection a crystal of dimensions $0.06 \times 0.08 \times 0.20$ mm was used. However, the Weissenberg photographs showed some splitting of the diffraction spots, indicating a crystal of poor quality. This feature was found for all the examined crystals. Three-dimensional data with $\theta \leq 25°$ were measured on the four-circle diffractometer (CAD-4F) using monochromated MoKα-radiation and ω-scan technique. A total of 5396 independent reflections was reduced to 2400 reflections with $I \geq 2$ σ (I). The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by Patterson technique.[6] The calculations included full-matrix least-squares refinements of positional and anisotropic, respectively isotropic, thermal parameters for non-hydrogen and hydrogen atoms. The atomic scattering factors for Cu, Cl, N and C are those given by Cromer and Mann,[7] and for H, those given by Stewart et al.[8] The weights were of the form $w^{-1} = a + b\sigma^2(F_o) + c|F_o| + d|F_o|^2$ with the coefficients adjusted to give as uniform a distribution of $w|\Delta F|^2$ as possible.[9] For the illustrations the PLUTO programme[10] was used. The space group $P\bar{1}$ was assumed in all calculations. The refinement confirms that this choice is correct.

Crystal data and R-values are listed in Table 1. The final positional parameters with estimated standard deviations are listed in Table 2 and the labelling of the BTAH-atoms are shown in Fig. 1.

Table 1. Crystal data.

M	763.4
$\mu(\text{Mo}K\alpha)\,(\text{cm}^{-1})$	17.8
Crystal system	triclinic
$V(\text{Å}^3)$	1536.8
$a(\text{Å})$	8.591(3)
$b(\text{Å})$	11.906(4)
$c(\text{Å})$	16.083(4)
$\alpha(°)$	110.62(5)
$\beta(°)$	91.95(5)
$\gamma(°)$	92.04(5)
Space group	$P\bar{1}$
$D_c(\text{g cm}^{-3})$	1.65
Z	2
$R = \sum \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \sum \lvert F_o \rvert$	0.053
$R_w = \left[\dfrac{\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2}{\sum w \lvert F_o \rvert^2} \right]^{\frac{1}{2}}$	0.063

Table 2. Atomic coordinates $\times 10^4$. The estimated standard deviations $\times 10^4$ are given in parantheses. The values for hydrogen atoms are multiplied by 10^3.

Atom	x	y	z
Cu1	6255(2)	1214(1)	25(1)
Cl1	6620(3)	−816(2)	−516(2)
Cl2	7021(4)	3165(3)	293(2)
Cu2	3756(2)	3938(1)	5165(1)
Cl3	3471(4)	6039(3)	5337(2)
Cl4	2308(7)	2400(4)	5307(2)
O1	5142(23)	596(14)	4295(8)
O2	8925(30)	427(19)	5007(13)
BTAH 1			
N1	7218(14)	2246(10)	2643(7)
N2	6500(12)	2205(8)	1874(5)
N3	7124(11)	1369(7)	1247(5)
C4	8284(12)	855(9)	1602(6)
C5	8337(13)	1456(9)	2510(7)
C6	9392(17)	1229(12)	3099(9)
C7	10385(18)	360(14)	2710(9)
C8	10385(19)	−244(14)	1794(11)
C9	9294(15)	−44(11)	1213(7)
H1	716(19)	265(13)	299(9)
H2	950(17)	174(13)	373(10)
H3	1110(15)	21(10)	299(8)
H4	1094(15)	−71(11)	160(8)
H5	929(12)	−43(9)	61(7)

Table 2. Continued.

BTAH 2			
N1	4650(12)	630(10)	−2504(6)
N2	5528(12)	388(8)	−1894(5)
N3	5182(11)	1158(8)	−1114(5)
C4	4056(14)	1882(10)	−1223(7)
C5	3700(15)	1543(11)	−2130(7)
C6	2580(27)	2126(19)	−2463(14)
C7	1874(22)	3033(15)	−1879(12)
C8	2210(21)	3394(14)	−984(13)
C9	3258(17)	2822(12)	−628(9)
H1	481(18)	8(14)	−300(10)
H2	251(14)	188(10)	−280(7)
H3	87(16)	344(11)	−197(8)
H4	147(17)	368(13)	−64(9)
H5	345(14)	295(10)	−7(8)
BTAH 3			
N1	4511(13)	5279(9)	7815(6)
N2	3964(13)	5281(8)	7034(6)
N3	4582(11)	4385(8)	6416(5)
C4	5583(15)	3826(10)	6832(7)
C5	5563(14)	4422(9)	7740(6)
C6	6452(17)	4081(12)	8346(9)
C7	7349(19)	3149(13)	8012(9)
C8	7434(17)	2591(13)	7104(10)
C9	6548(18)	2887(13)	6499(9)
H1	441(15)	584(11)	828(8)
H2	620(17)	444(13)	883(9)
H3	786(15)	300(11)	837(8)
H4	808(14)	208(10)	697(7)
H5	661(17)	253(13)	608(9)
BTAH 4			
N1	3070(12)	2297(9)	2543(5)
N2	3662(12)	2470(9)	3354(6)
N3	2988(12)	3397(8)	3904(5)
C4	1938(14)	3807(9)	3430(6)
C5	1964(14)	3070(10)	2544(6)
C6	1035(16)	3211(11)	1871(7)
C7	70(18)	4103(12)	2125(9)
C8	−52(18)	4870(15)	3025(10)
C9	851(16)	4683(11)	3676(8)
H1	337(13)	180(10)	207(7)
H2	109(12)	260(9)	123(7)
H3	−75(12)	422(8)	191(6)
H4	−75(18)	528(13)	309(10)
H5	72(11)	504(8)	417(6)

Lists of thermal parameters and observed and calculated structure factors may be obtained from the authors on request.
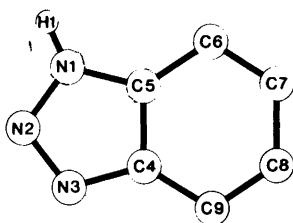
Fig. 1. The benzotriazole molecule.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Bond lengths and bond angles with their estimated standard deviations are listed in Tables 3 and 4.

The structure consists of two independent dimeric $[Cu(BTAH)_2Cl_2]_2$ units as shown in Fig. 2. The $Cu\underset{Cl'}{\overset{Cl}{<}}{>}Cu'$ bridging units are strictly planar, owing to the presence of the crystallographic inversion centers in the middle of the dimers. The geometry around each copper atom is approximately trigonal bipyramidal, the equatorial atoms being three chlorine atoms (Fig. 3). The axial sites are occupied by nitrogen atoms (N3) from two different BTAH ligands. The Cu-atom and the three equatorial atoms are nearly coplanar, the deviations from their least-squares planes being less than 0.02 Å. The angles between the normal of this "trigonal" plane and the two planes through the BTAH ligands are 89.9 and 86.4° for the Cu1-dimer, and 87.7 and
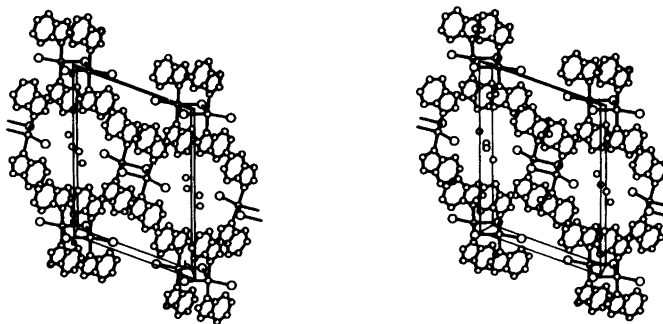
Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations in the Copper Coordination Spheres. Primed atoms are related to unprimed atoms by a crystallographic inversion center. The figures in parentheses refer to the numbers of the BTAH ligands.

Atoms	Distance or angle	Atoms	Distance or angle
Cu1 – Cl1	2.299(3)	Cu2 – Cl3	2.441(4)
Cu1 – Cl1′	2.694(4)	Cu2 – Cl3′	2.544(4)
Cu1 – Cl2	2.277(4)	Cu2 – Cl4	2.260(6)
Cu1 – N3(1)	2.020(9)	Cu2 – N3(3)	1.989(8)
Cu1 – N3(2)	2.002(9)	Cu2 – N3(4)	1.980(8)
Cl1 – Cu1 – Cl1′	90.7(1)	Cl3 – Cu2 – Cl3′	92.5(1)
Cl2 – Cu1 – Cl1′	116.4(1)	Cl4 – Cu2 – Cl3′	129.0(2)
Cl1 – Cu1 – Cl2	152.9(2)	Cl3 – Cu2 – Cl4	138.5(2)
N3(1) – Cu1 – Cl1	91.6(3)	N3(3) – Cu2 – Cl3	91.9(3)
N3(1) – Cu1 – Cl1′	89.3(3)	N3(3) – Cu2 – Cl3′	89.7(3)
N3(1) – Cu1 – Cl2	89.9(3)	N3(3) – Cu2 – Cl4	89.9(3)
N3(2) – Cu1 – Cl1	92.5(3)	N3(4) – Cu2 – Cl3	91.4(3)
N3(2) – Cu1 – Cl1′	85.5(3)	N3(4) – Cu2 – Cl3′ ·	89.0(3)
N3(2) – Cu1 – Cl2	88.8(3)	N3(4) – Cu2 – Cl4	88.3(3)
N3(1) – Cu1 – N3(2)	173.4(3)	N3(3) – Cu2 – N3(4)	176.5(6)
Cu1 – Cl1 – Cu1′	89.3(1)	Cu2 – Cl3 – Cu2′	87.5(1)

Fig. 2. Stereo view along the *a*-axis of the structure.

Table 4. Bond distances (Å) and bond angles (°) with estimated standard deviations in the BTAH ligands.

Atoms	BTAH 1 Distance or angle	BTAH 2 Distance or angle	BTAH 3 Distance or angle	BTAH 4 Distance or angle
N1 – N2	1.347(15)	1.334(15)	1.327(14)	1.328(13)
N2 – N3	1.290(11)	1.318(11)	1.318(12)	1.315(12)
N3 – C4	1.395(15)	1.365(16)	1.394(17)	1.370(16)
C4 – C5	1.379(13)	1.389(16)	1.381(14)	1.388(12)
C5 – N1	1.338(17)	1.359(16)	1.363(16)	1.345(16)
C5 – C6	1.390(20)	1.401(29)	1.396(20)	1.383(17)
C6 – C7	1.354(20)	1.337(26)	1.335(21)	1.328(19)
C7 – C8	1.392(20)	1.366(27)	1.380(20)	1.425(18)
C8 – C9	1.385(22)	1.373(26)	1.364(24)	1.366(22)
C9 – C4	1.386(16)	1.409(17)	1.379(19)	1.386(17)
N1 – H1	0.60(12)	0.86(14)	0.81(11)	0.84(10)
C6 – H2	0.99(13)	0.52(9)	0.79(14)	1.04(9)
C7 – H3	0.80(13)	1.03(14)	0.79(14)	0.82(11)
C8 – H4	0.74(13)	0.85(15)	0.81(12)	0.78(16)
C9 – H5	0.91(10)	0.87(12)	0.67(12)	0.77(9)
C5 – N1 – N2	112.1(9)	112.0(9)	113.1(8)	112.4(8)
N1 – N2 – N3	106.5(1.0)	106.6(9)	107.0(1.0)	107.0(1.0)
N2 – N3 – C4	110.2(8)	110.0(9)	108.5(8)	109.1(8)
N3 – C4 – C5	106.2(9)	107.4(9)	108.2(1.0)	107.6(9)
C4 – C5 – N1	104.9(1.0)	104.0(1.1)	103.2(1.0)	103.8(9)
C4 – C5 – C6	123.6(1.1)	121.4(1.2)	122.3(1.1)	123.6(1.1)
C5 – C6 – C7	114.4(1.1)	117.9(1.8)	117.1(1.2)	115.7(1.0)
C6 – C7 – C8	123.3(1.5)	122.1(2.0)	120.8(1.6)	123.6(1.4)
C7 – C8 – C9	121.9(1.4)	122.0(1.5)	123.1(1.4)	119.1(1.4)
C8 – C9 – C4	115.2(1.0)	117.6(1.4)	116.8(1.2)	118.8(1.1)
C9 – C4 – C5	121.3(1.1)	119.0(1.2)	119.7(1.2)	118.9(1.1)

81.8° for the Cu2-dimer. The angles between the normals of the BTAH ligands are 4.6° (Cu1-dimer) and 6.2° (Cu2-dimer). The distortion from trigonal bipyramidal geometry is largest for the Cu1-dimer, and the coordination around Cu1 may alternatively be described as square pyramidal with Cl1′ axial and Cl1, Cl2, N3(1) and N3(2) in the base plane. The distortion from this geometry is not much greater than distortion from the trigonal bipyramidal geometry. For the Cu2-dimer the distortion from
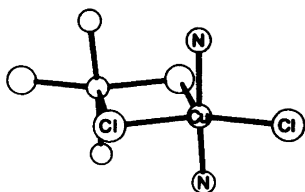

Fig. 3. The coordination around the Cu-atoms. A crystallographic inversion center is present in the middle of the dimer.

trigonal bipyramidal geometry is much smaller than the distortion from square pyramidal geometry. The average deviations of the four basal atoms from the least-squares plane through them are 0.32 and 0.43 Å for the Cu1-dimer and the Cu2-dimer, respectively. The Cu1 atom is 0.22 Å out of plane, whereas the Cu2 atom is 0.40 Å out of plane. Therefore, the geometry around the copper atoms is more readily described as being a distorted trigonal bipyramid.

The terminal Cu – Cl distances of 2.277(4) and 2.260(6) Å are shorter than the bridging Cu – Cl distances [2.299(3), 2.694(4), 2.441(4), and 2.544(4) Å], which fall within the range of 2.3 – 3.2 Å found in other metal-chloride bridged systems.[11] The bridged Cu – Cl distances show the commonly observed asymmetry;[12] there are stronger Cu – Cl bonds (2.3 – 2.4 Å) and weaker ones (2.5 – 2.7 Å). The Cl – Cl′ separations, 3.564(4) Å for the Cu1-dimer and 3.602(5) Å for the Cu2-dimer, are quite large, but in agreement with the values (3.4 – 3.6 Å)

reported for other trigonal bipyramidal copper dimers.[13,14] Contrary to the Cl−Cu−Cl' angles in the latter dimers, the Cl−Cu−Cl' angles in the present structure are obtuse [90.7(1) and 92.5(1)°].

There is no copper−copper bond in the dimers. The Cu−Cu distances are 3.520(2) Å in the Cu1-dimer and 3.448(3) Å in the Cu2-dimer. These separations are in agreement with the Cu−Cu distance of 3.575 Å found in $(C_5H_6N_5O)CuCl_3 \cdot H_2O$,[13] but somewhat shorter than the 3.722 Å reported for $[Co(N_2C_2H_8)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$.[14] The Cu−N bonds of $1.98-2.02$ Å fall within values of Cu−N distances normally found in copper complexes.

The BTAH ligands are nearly planar, the deviations of the atoms from the least-squares planes through them being less than 0.04 Å. The metrical details of the BTAH ligands in the present complex are compared with those of benzotriazole[15] in Table 5. The bond lengths and bond angles in an average group were found as weighted averages of the independent quantities. The variance, σ^2, of the weighted mean was calculated from $\sigma^2 = \frac{1}{n-1}\sum w_i \Delta_i^2 / \sum w_i$, where Δ_i are the residuals and w_i the weights. For the copper complex the weights were chosen in accordance with the estimated standard deviations of the bond lengths and bond angles, whereas unit weights are used in the case of benzotriazole. The reason for this is that the origin in the polar space group was fixed by keeping some positional parameters invariant, leading to artifically low standard deviations for some of the bond lengths and bond angles. The agreement between the two average molecules is quite good, indicating that coordination to the metal has only a small effect on the geometry of the benzotriazole molecule.[5]

Similar results are found in tetrachlorobis-2-[(5-amino-4-carboxamidinium)[1,2,3]triazole]copper (II) monohydrate,[16,17] and in dichlorobis(benzo-triazole)zinc(II).[4]

The packing of the structure is shown in Fig. 2. The Cu1−Cu1'-line lies almost in the $ab0$-plane ($z \sim 0$ for Cu1), the angles between the Cu_2Cl_4-plane and the ab- and ac-plane being 26.2 and 86.1°, respectively. For the Cu2-dimer, the Cu2−Cu2'-line lies almost in the $ab\frac{1}{2}$-plane ($z \sim \frac{1}{2}$ for Cu2), the corresponding angles being 17.9 and 74.1°, respectively. Between the two "Cu−Cl"-planes the angle is 12.3°.

Table 5. Comparison of the BTAH ligand in $[Cu(BTAH)_2Cl_2]_2.H_2O$ with benzotriazole. Average values of four independent molecules for both compounds.

Distance (Å) or angle (°)	$[Cu(BTAH)_2Cl_2]_2 \cdot H_2O$	Benzotriazole[15]
N1−N2	1.333(5)	1.346(5)
N2−N3	1.310(7)	1.310(4)
N3−C4	1.381(8)	1.377(6)
C4−C5	1.384(2)	1.389(5)
C5−N1	1.352(6)	1.366(7)
C5−C6	1.390(4)	1.404(4)
C6−C7	1.338(6)	1.367(3)
C7−C8	1.396(13)	1.405(5)
C8−C9	1.372(5)	1.368(5)
C9−C4	1.390(6)	1.409(5)
C5−N1−N2	112.4(3)	110.3(7)
N1−N2−N3	106.8(1)	108.8(4)
N2−N3−C4	109.4(4)	108.2(2)
N3−C4−C5	107.3(4)	108.4(2)
C4−C5−N1	104.0(4)	104.2(4)
C4−C5−C6	122.8(5)	122.7(4)
C5−C6−C7	115.9(7)	115.3(3)
C6−C7−C8	122.6(7)	122.7(1)
C7−C8−C9	121.5(9)	122.2(2)
C8−C9−C4	117.0(8)	116.2(4)
C9−C4−C5	119.8(6)	120.9(2)

The two "Cu−Cl"-planes are separated by layers of almost parallel BTAH ligands, the angles between them being in the range of $3-8°$. The angles between the BTAH ligands and the *ab*-plane lie in the range of $83-89°$. Between the Cu2-dimers statistically disordered water molecules are situated.

The shortest non-bonded distance between the BTAH ligands in the Cu1-dimer are found between BTAH1 and BTAH2′. These are the N3−N2 distance of 3.47 Å, the C5−N1 distance of 3.51 Å and the C9−C4 distance of 3.56 Å. The corresponding distances in the Cu2-dimer are found between BTAH3 and BTAH4′. These are the N3−N3 distance of 3.50 Å and the N3−C4 distance of 3.57 Å.

Between the two dimers the shortest intermolecular distances are found between N2(BTAH1) and N1(BTAH4) (3.16 Å) and between C7(BTAH3) and C5(BTAH2 $(x,y,z+1)$) (3.57 Å). These distances are somewhat shorter than those (3.62−3.68 Å) found between BTA molecules in TlBTA.[18] From Cl2 (Cu1-dimer) the shortest distance (3.30 Å) is found to N1(BTAH3′). The shortest distances from Cl4 (Cu2-dimer) are 3.37 and 3.35 Å to O1 and O2 $(1-x,-y,1-z)$, respectively. The only hydrogen bond (2.75 Å) is found between N1(BTAH2) and O1 $(1-x,-y,-z)$.

Investigations on the nature of the protective layers on copper[1,18] have revealed that there are substantial differences in both composition and structure of BTA films formed on copper, depending on the valence state of the metal. The Cu(I) compound seems to have the approximate composition CuBTA, while the Cu(II) compound appears to be more complex and to be stabilized by the presence of water and anions such as chloride.

Although the present structure hardly is the Cu(II) compound of the protecting BTA film on copper, it shows that BTAH ligands can be arranged in such a way that the copper surface is well covered. The same feature has not been found in $Zn(BTAH)_2Cl_2$.[4]

REFERENCES

1. Fox, P. G., Lewis, G. and Boden, P. J. *Corros. Sci. 19* (1979) 457, and references therein.

2. Meunier-Piret, J., Piret, P., Putzeys, J.-P. and Van Meerssche, M. *Acta Crystallogr. B 32* (1976) 714.
3. Brown, L. D., Ibers, J. A. and Siedle, A. R. *Inorg. Chem. 17* (1978) 3026.
4. Søtofte, I. and Nielsen, K. *Acta Chem. Scand. A 35* (1981) 739.
5. Søtofte, I. and Nielsen, K. *Acta Chem. Scand. A 35* (1981) 747.
6. Stewart, J. M., Kundell, F. A. and Baldwin, J. C. *The X-Ray System, Version of 1975*, University of Maryland, College Park 1975.
7. Cromer, D. and Mann, J. B. *Acta Crystallogr. A 24* (1968) 321.
8. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
9. Nielsen, K. *Acta Crystallogr. A 33* (1977) 1009.
10. Motherwell, W. D. S. *PLUTO*, University of Cambridge, England 1976.
11. Willett, R. D. and Rundle, R. E. *J. Chem. Phys. 40* (1964) 838.
12. Colton, R. and Canterford, J. H. *Halides of the First Row Transition Metals*, Wiley−Interscience, New York 1969.
13. Carrabine, J. A. and Sundaralingam, M. *J. Am. Chem. Soc. 92* (1970) 369.
14. Hodgson, D. J., Hale, P. K. and Hatfield, W. E. *Inorg. Chem. 10* (1971) 1061.
15. Escande, A., Galigné, J. L. and LaPasset, J. *Acta Crystallogr. B 30* (1974) 1490.
16. Purnell, L. G., Shepherd, J. C. and Hodgson, D. J. *J. Am. Chem. Soc. 97* (1975) 2376.
17. Nielsen, K. and Søtofte, I. *To be published.*
18. Reedijk, J., Roelofsen, G., Siedle, A. R. and Spek, A. L. *Inorg. Chem. 18* (1979) 1947, and references therein.