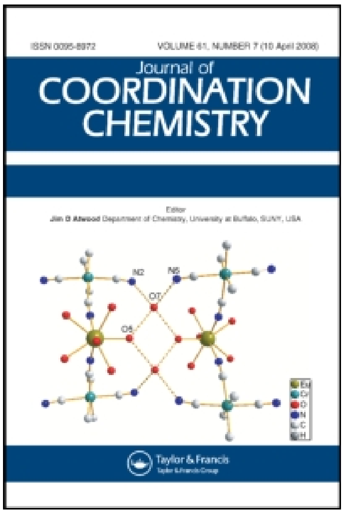

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CRYSTAL STRUCTURE AND PROPERTIES OF A COPPER(II) COMPLEX OF AN 18-MEMBERED MACROCYCLIC LIGAND WITH *N,N'* - DICARBOXYLIC ACID ARMS

Yin-Han Zhang[a]; Yu-Peng Tian[b]; Fu-Xin Xie[b]; Zu-Yao Chen[a]; De-Liang Long[c]; Jiu-Tong Chen[c]; Jin-Shun Huang[c]
[a] Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui, China [b] Department of Chemistry, Anhui University, Hefei, Anhui, China [c] Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, China

To cite this Article Zhang, Yin-Han , Tian, Yu-Peng , Xie, Fu-Xin , Chen, Zu-Yao , Long, De-Liang , Chen, Jiu-Tong and Huang, Jin-Shun(1999) 'CRYSTAL STRUCTURE AND PROPERTIES OF A COPPER(II) COMPLEX OF AN 18-MEMBERED MACROCYCLIC LIGAND WITH *N,N'* -DICARBOXYLIC ACID ARMS', Journal of Coordination Chemistry, 47: 2, 289 — 297

To link to this Article: DOI: 10.1080/00958979908023061

URL: http://dx.doi.org/10.1080/00958979908023061

J. Coord. Chem., 1999, Vol. 47, pp. 289–297
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

CRYSTAL STRUCTURE AND PROPERTIES OF A COPPER(II) COMPLEX OF AN 18-MEMBERED MACROCYCLIC LIGAND WITH *N,N′*-DICARBOXYLIC ACID ARMS

YIN-HAN ZHANG[a,*], YU-PENG TIAN[b], FU-XIN XIE[b],
ZU-YAO CHEN[a], DE-LIANG LONG[c], JIU-TONG CHEN[c]
and JIN-SHUN HUANG[c]

[a]*Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China;* [b]*Department of Chemistry, Anhui University, Hefei, Anhui 230039, China;* [c]*Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, China*

(Received 9 April 1998)

$CuL \cdot 5H_2O$ (H_2L = 1,15-diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclo-octadecane-*N,N′*-diacetic acid) crystallized from water. Its crystal structure was determined by X-ray diffraction analysis and refined in space group *Pnma*, $a = 20.1784(11)$, $b = 15.8745(9)$, $c = 8.9266(5)$ Å, $V = 2859.4(3)$ Å^3, $Z = 4$, $\lambda(\text{MoK}\alpha) = 0.71073$, $R_w = 0.0294$ for 1822 observed reflection [$I > 2\sigma(I)$]. The copper atom is surrounded by two nitrogen atoms, two oxygen atoms from the carboxyl groups in the ligand and one oxygen atom from a coordinated water to form a distorted square pyramidal arrangement. The three ether oxygen atoms in the cycle have no contact with the copper ion.

The stability constant for the 1 : 1 complex of copper(II) and protonation constants for the ligand have been determined by potentiometric titration in water ($I = 0.1$, KNO_3) at 25°C. Electronic spectra, conductivity measurements, thermal analysis, and the EPR of the complex are discussed in terms of the crystal structure.

Keywords: Crystal structure; macrocyclic ligand; metal complexes; stability constants

INTRODUCTION

Selective complexation of macrocyclic ligands with specific metal ions is an important and rapidly expanding area of research.[1] For example,

---

[*] Corresponding author.

1,4,8,11-tetraazacyclotetradecane-N,N',N'',N'''-tetracarboxylic acid has been demonstrated to form an unusually stable complex with calcium. A number of mixed oxygen and nitrogen donor macrocyclic derivatives with pendant carboxylic acid groups have been developed and their complexing properties investigated in recent years. Macrocyclic systems with one,[2] two or three[3–6] and four[7] pendant acid groups have also been studied. Their specific complexation behaviour is clearly of interest in many areas such as the design of potential lanthanide ion selective reagents[8,9] and of complexes to act as medical imaging agents[10] and to treat heavy metal intoxication.[11,12]

We have reported the synthesis and characterization of a series of macrocyclic ligands.[2,3] However, the stereochemistry and properties of the copper complexes are still unresolved. In this paper, we describe the structure of a copper complex ($CuL \cdot 5H_2O$), the protonation constants of ligand L, stability constants of the copper complex, and other properties of the complex.

EXPERIMENTAL

All chemical reagents were commercial products of analytical grade. Solvents were purified by conventional methods. The parent macrocycle and its copper complex were prepared according to methods previously reported.[3]

Potentiometric Determination

The potentiometric apparatus consisted of a water-jacketted measuring cell with glass electrode and a water-jacketted calomel reference electrode connected through a salt bridge. A common supporting electrolyte with ionic strength $0.100\,\mathrm{mol\,dm^{-3}}$ adjusted by KCl or KNO_3 was used and the temperature was maintained at $25 \pm 0.1°C$.

Potentiometric measurements and computation of the protonation and stability constants were carried out by procedures described elsewhere.[13] Typical concentrations of experimental solutions were $2.00 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ of H_2L and $0.100\,\mathrm{mol\,dm^{-3}}$ of KOH, and initial solution volumes were $50.0\,\mathrm{cm^3}$. Twenty experimental data points were recorded by titration for measurement of protonation constants. Three parallel titrations were performed. Standard stock solutions were prepared from analytical grade $Cu(NO_3)_2$. The meter-glass electrode system was calibrated by standard acid with KCl at $0.100\,\mathrm{mol\,dm^{-3}}$ as supporting electrolyte to read hydrogen ion concentration directly so that the measured value was $-\log[H^+]$.

Crystal Structure Determination

Blue single crystals of $CuL(H_2O) \cdot 5H_2O$ were obtained from water. A crystal with dimensions $0.9 \times 0.5 \times 0.1$ mm was mounted on a glass fibre and scanned on a Siemens SMART-CCD area-detecting diffractometer equipped with graphite – monochromated MoKα ($\lambda = 0.71073$) radiation. Intensity data were obtained by using an ω scan mode with a scan speed of 10 seconds/frame and 0.3°/frame in the range of $2.02° < \theta < 23.4°$. Data reduction and cell refinement were prerformed with SMART[14] and SAINT[15] software. The cell parameters were obtained from a least-squares fit of 135 reflections ($3.05 < \theta < 20.27$).

A total of 2134 unique reflections was collected and 1822 observed reflections with $I > 2\sigma(I)$ were used in the structure determination. All calculations were performed on a Silicon Graphics Indy workstation with the SHELXTL program.[16] The structure was solved by direct methods. All non-hydrogen atoms were located on an E-map or in successive difference Fourier syntheses. Non-hydrogen atom scattering factors were taken from Cromer and Waber.[17] The structure was refined by full-matrix least-squares techniques based on F^2. Hydrogen atoms were located theoretically and not refined. The final cycle of full-matrix least-squares refinement converged with $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.029$ and $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]] = 0.076$, $w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 1.1783P]$, where $P = (F_o^2 + 2F_c)/3$. The largest and smallest peak in the final difference Fourier map had a height of 0.165 and -0.267 e/Å^3. Crystal data together with some experimental details are listed in Table I.

TABLE I Crystal and experimental data for $CuL \cdot 5H_2O$

Empirical formula	$CuC_{25}H_{40}O_{12}N_2$
M	624.13
Crystal size (mm)	$0.9 \times 0.5 \times 0.1$
Crystal system	Orthorhombic
Space group	*Pnma*
a (Å)	20.1784(11)
b (Å)	15.8745(9)
c (Å)	8.9266(5)
Volume (Å^3)	2859.4(3)
Z	4
Density (calculated)	1.450 Mg m^{-3}
Absorption correction	ASDABS[23]
Transmission factors	0.754–1.000
Radiation (λ, Å)	MoKα (0.71069)
Temperture (K)	293(2)
Unit reflections	2134
Observed reflections	1822
R	0.0294
R_w	0.0757

RESULTS AND DISCUSSION

Protonation and Stability Constants

The protonation constants were determined potentially by titrating the respective ligand hydrochlorides with base, where

$$K_1 = [H_4L^{2+}]/[H_3L^+][H^+] \quad K_2 = [H_3L^+]/[H^+][H_2L]$$
$$K_3 = [H_2L]/[HL^-][H^+].$$

For ligand L, $\log K_1$ and $\log K_2$ are 10.35(1) and 7.68(1), which refer to the protonation of the amine groups; $\log K_3$ is 2.0(3), corresponding to protonation of one carboxylic function. Further eveidence that K_1 and K_2 correspond to protonation at the amine sites is given by the fact that their respective magnitudes do not differ greatly from the corresponding values for the parent macrocycles.[6]

The interaction of the ligand L with Cu(II) has been studied in aqueous solution ($I = 0.1$ KNO_3, 25°C). The stability constant for the 1 : 1 (molar ratio of metal and ligand) complex is $2.6(3) \times 10^{18}$. The data confirm that the carboxylic arms participate in the formation of the complex since the observed $\log K$ value is considerably greater than those of corresponding complexes of precursor O_3N_2 macrocycles found previously.[18]

Electronic and EPR Spectra

The electronic spectrum of the copper complex was recorded in DMF solution. In the electronic spectrum of the ligand a band at 276 nm, $\varepsilon = 854\,M^{-1}\,cm^{-1}$, is assigned to a π–π^* transition. Since this is only slightly affected by coordination of the ligand to copper(II), the maximum absorbtion of the complex is at 278 nm ($\varepsilon = 115\,M^{-1}\,cm^{-1}$). At the same time, the complex has a maximum at 612 nm (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) and a shoulder at 750 nm ($d_{z^2} \rightarrow d_{x^2-y^2}$). The data agree with those of other square pyramidal systems reported previsouly.[19,20]

The EPR spectrum in DMF at room temperature shows a line shape characheristic of a complex with $g_{iso} = 2.057$, but information on the electronic ground state is unobserved. The spectrum of the complex in the glass state at 77 K shows four intense peaks due to copper hyperfine lines, $g_\perp =$ 2.006, $A_\perp = 0.0195\,cm^{-1}$, and an intense transition with $g_\parallel = 2.240$, $A_\parallel =$ $0.0188\,cm^{-1}$. The fact that $g_\parallel > g_\perp$ is in agreement with square pyramidal stereochemistry.[20] At high magnetic fields, there are five super hyperfine lines in the spectrum of the complex at 77 K owing to coincident activity between copper and nitrogen atoms.[21]

Thermal Analysis

Thermal measurements were determined in air. The TG curve shows that the complex loses its five water molecules (obs. 13.9%, calc. 14.4%) from 89°C to 156°C. The loss of coordinated and non-coordinated water could not be distinguished. An endotherm at 102°C is assigned to loss of water molecules and two exotherms occur at 203°C and 241°C in the DTA curve of the complex. Because the melting point of the complex is 246.5°C, one exothermic peak is divided into two by this endothermic process. The TG curve shows the complex loses weight (18.5%) owing to decomposition of ligand and loss of the two pendant carboxylic groups (calc. 19.2%). After the complex was heated for 30 min at 255°C, the residue had no peak in the region 1750–1600 cm^{-1} as measured by IR. Breakdown of the macrocycle occurs at 468°C and complete decomposition at 507°C.

Crystal Structure

Final atomic coordinates and equivalent thermal parameters of non-hydrogen atoms are listed in Table II, and main bond lengths and angles in Table III. The crystal structure shows the copper complex consists of the copper(II) ion, a deprotonated ligand, one coordinated water molecule and four molecules of crystalline water. The three ether oxygen atoms of the macrocyclic ligand are not coordinated with the metal ion. A perspective view of the structure and the packing of molecules in the unit cell are shown in Figures 1 and 2.

The structure determination demonstrates that the coordination number of copper is five. Two nitrogen atoms in the macrocyclic ligand and two oxygen atoms O(1), O(1^*) from carboxyl groups lies in a plane: with the pyramidal coordination sphere completed by the oxygen atom from a water molecule.

The two equivalence Cu–N and Cu–N^* bonds (Table III) are in the normal range for Cu-amine distances (1.957–2.08 Å),[2,22–24] and both of Cu–O bonds fall within the range of values (1.88–2.24) reported for five-coordinate copper(II) complexes which have carboxyl group donor.[2,24,25] The apical Cu–O bond is slightly longer, 2.346(3) Å. The coordinated water forms an H-bond with O(11) and with O(4) from an adjacent molecule to

TABLE II Atomic, coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for the complex

Atom	*x/a*	*y/b*	*z/c*	B_{eq}	*Atom*	*x/a*	*y/b*	*z/c*	B_{eq}
Cu	1945(1)	7500	8490(1)	39(1)	C(4)	1218(1)	8305(2)	5945(3)	51(1)
N	1459(1)	8470(1)	7504(1)	40(1)	C(5)	823(2)	7500	5785(4)	52(3)
O(0)	2880(2)	7500	6929(4)	65(1)	C(6)	−872(2)	9009(4)	6126(6)	95(2)
O(1)	2361(1)	8404(1)	9646(2)	47(1)	C(7)	−963(2)	8247(4)	5226(5)	104(2)
O(2)	2641(1)	9751(1)	9521(2)	64(1)	C(11)	597(1)	9592(2)	8304(3)	54(1)
O(3)	−225(1)	8980(2)	6790(3)	79(1)	C(12)	856(2)	10293(2)	9014(4)	68(1)
O(4)	−965(1)	7500	6129(3)	73(1)	C(13)	564(2)	11081(2)	8898(5)	85(1)
O(11)	3050(2)	7500	3971(4)	90(1)	C(14)	−16(2)	11156(3)	8096(6)	99(2)
O(12)	−1322(2)	12500	7995(4)	76(1)	C(15)	−295(2)	10482(3)	7422(5)	89(1)
O(13)	2714(2)	11196(2)	7742(3)	90(1)	C(16)	12(1)	9692(2)	7473(4)	69(1)
C(1)	2357(1)	9113(2)	8962(3)	48(1)	C(2)	1980(1)	9129(2)	7487(3)	45(1)
C(3)	899(1)	8730(2)	8542(3)	44(1)					
H(0A)	2972(21)	7500	5994(56)	68(14)	H(0B)	3171(22)	7500	7258(51)	57(16)
H(11)	2832(23)	7867(26)	3648(47)	119(17)	H(21)	−1536(17)	12061	7757(40)	89(11)
H(31)	2678(19)	10762(19)	8106(44)	87(15)	H(32)	2571(21)	11145(27)	6946(50)	108(16)
H(2A)	2276(13)	8992(16)	6770(28)	47(7)	H(2B)	1804(11)	9683(15)	7301(25)	38(6)
H(3A)	581(11)	8308(13)	8484(22)	29(6)	H(3B)	1086(11)	8717(14)	9524(29)	45(7)
H(4A)	1607(12)	8275(14)	5324(28)	50(7)	H(4B)	960(13)	8798(16)	5674(28)	50(7)
H(5A)	643(17)	7500	4735(45)	53(10)	H(5B)	460(20)	7500	6378(41)	52(11)
H(6A)	−923(19)	9554(25)	5542(47)	120(14)	H(6B)	−1182(18)	9053(20)	6939(38)	84(11)
H(7A)	−645(17)	8146(19)	4542(39)	87(11)	H(7B)	−1370(18)	8294(20)	4737(38)	93(10)
H(12)	1259(14)	10217(16)	9615(29)	56(8)	H(13)	752(16)	11515(21)	9319(37)	77(12)
H(14)	−219(20)	11640(25)	8024(42)	105(13)	H(15)	−688(19)	10515(22)	6886(38)	92(16)

form a two dimensional network. There are many H-bonds between the coordinated water, crystalline water, carboxylic oxygen and ether oxygen atoms. O–O distances of hydrogen bonds are listed in Table III. Hydrogen bonds in a unit cell are illustrated in Figure 2.

Ether oxygen atoms of parent macrocycles with mixed oxygen and nitrogen atoms coordinate with copper and nickel,[26,27] but not with zinc and cadium.[28-30] Ether oxygen atoms of macrocyclic ligands with carboxyl acid groups[2,3] do not coordinate with copper and nickel. These results provide evidence that the amine nitrogen atoms in macrocyclic ligands coordinate with metal ions more easily that the ether oxygen atoms.

Acknowledgments

This work was supported by the Youth Fund of the University of Science and Technology of China, the Anhui Provincial Natural Science Fund and the Research Fund of the State Key Laboratory of Coordination Chemistry at Nanjing University.

TABLE III Selected bond distances (Å) and bond angles (°)

Cu–O(1)	1.958(2)	Cu–O(1*)	1.958(2)	Cu–N	2.027(2)	Cu–N*	2.028(2)
Cu–O	2.346(3)	N–C(2)	1.484(3)	N–C(4)	1.497(3)	N–C(3)	1.518(3)
O(1)–C(1)	1.279(3)	O(2)–C(1)	1.234(3)	O(3)–C(16)	1.371(4)	O(3)–C(6)	1.434(4)
O(4)–C(7*)	1.434(5)	O(4)–C(7)	1.434(5)	C(1)–C(2)	1.521(4)	C(3)–C(11)	1.513(4)
C(4)–C(5)	1.513(4)	C(5)–C(4*)	1.513(3)	C(6)–C(7)	1.463(6)	C(11)–C(12)	1.383(5)
C(11)–C(16)	1.403(4)	C(12)–C(13)	1.387(4)	C(13)–C(14)	1.376(7)	C(14)–C(15)	1.351(6)
C(15)–C(16)	1.399(5)						
O···O	2.663(3)	O(2)···O(13)	2.745(4)	O(1)···O(13)[a]	2.839(3)		
O···O(14)[b]	2.905(3)	O(12)···O(13)[c]	2.195(4)	O(11)···O(13)[c]			
O(1)–Cu–O(1*)	94.33(10)	O(1)–Cu–N*	173.63(7)	O(1*)–Cu–N*	83.07(7)		
O(1)–Cu–N	83.07(7)	O(1*)–Cu–N	173.63(7)	N*–Cu–N	98.90(11)		
O(1)–Cu–O(0)	88.14(7)	O(1*)–Cu–O(0)	84.14(8)	N*–Cu–O(0)	97.57(8)		
N–Cu–O(0)	97.57(8)	C(2)–N–C(4)	110.1(2)	C(2)–N–C(3)	110.0(2)		
C(4)–N–C(3)	112.0(2)	C(2)–N–Cu	101.35(14)	C(4)–N–Cu	115.3(2)		
C(3)–N–Cu	107.57(14)	Cu–O(1)–C(1)	113.0(2)	C(16)–O(3)–C(6)	118.3(3)		
C(7*)–O(4)–C(7)	111.6(5)	O(2)–C(1)–O(1)	124.1(2)	O(2)–C(1)–C(2)	120.3(3)		
O(1)–C(1)–C(2)	115.6(2)	N–C(2)–C(1)	109.4(2)	C(11)–C(3)–N	117.4(2)		
N–C(4)–C(5)	114.0(2)	C(4)–C(5)–C(4*)	115.2(5)	O(3)–C(6)–C(7)	108.3(4)		
O(4)–C(7)–C(6)	112.0(3)	C(12)–C(11)–C(16)	118.0(3)	C(12)–C(11)–C(3)	120.7(2)		
C(16)–C(11)–C(3)	121.0(3)	C(11)–C(12)–C(13)	122.0(4)	C(14)–C(13)–C(12)	118.6(5)		
C(15)–C(14)–C(13)	121.2(4)	C(14)–C(15)–C(16)	120.7(4)	O(3)–C(16)–C(15)	124.8(4)		
O(3)–C(16)–C(11*)	115.8(3)	C(15)–C(16)–C(11)	119.4(4)				

Symmetry codes: * $x, -y-\frac{1}{2}, z$; [a] $\frac{1}{2}-x, -y, \frac{1}{2}+z$; [b] $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; [c] $\frac{1}{2}+x, y, \frac{1}{2}-z$; [d] $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$.

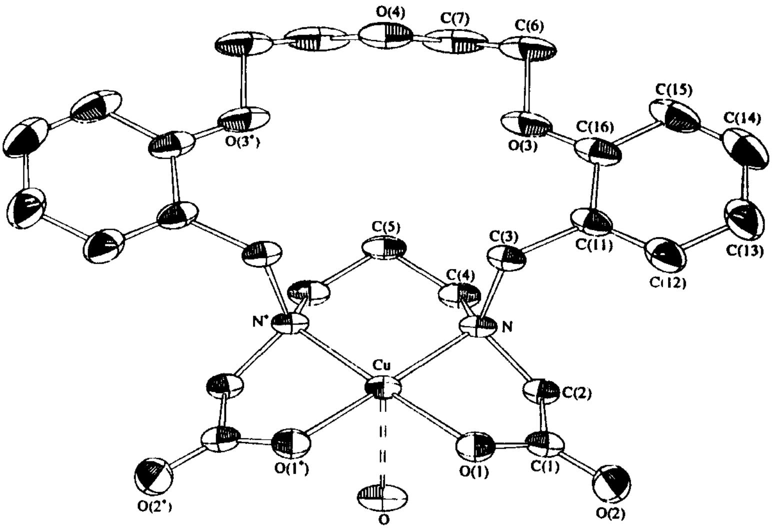

FIGURE 1 Molecular structure of the copper complex.

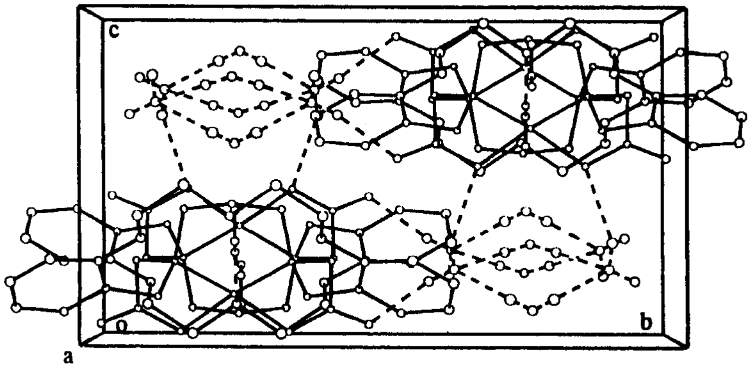

FIGURE 2 Packing diagram of molecules in unit cell viewed down the *c* axis.

Supplementary Material

Full list of crystallographic data are available from the authors upon request.

References

[1] (a) F.C.J.M. Van Veggel, W. Verboom and D.N. Reinhoudt, *Chem. Rev.* **94**, 279 (1994); (b) R.D. Hancock, *J. Chem. Educ.* **69**, 615 (1992).

[2] J.Y. Wu, F.X. Xie, Y.P. Tian, Y. Chen and S.S. Ni, *Chinese J. Struct. Chem.* **14**, 250 (1995).

[3] J.D. Xu, S.S. Ni, K.S. Cui and Z.Q. Zhi, *Inorg. Chim. Acta* **239**, 171 (1990).

[4] A.A. Warson, A.C. Willis and D.P. Fairlie, *Inorg. Chem.* **36**, 752 (1997).

[5] J. Huskens, D.A. Torres and Z. Kovacs, *Inorg. Chem.* **36**, 1495 (1997).

[6] K.R. Adam, A.J. Leong, L.F. Lindoy, P. Hendry, S.V. Smith and D. Yellowlees, *J. Coord. Chem.* **19**, 189 (1988).

[7] X.Y. Xu, M. Lan, Q.H. Lou and S.S. Ni, *Synth. React. Inorg. Met.-Org. Chem.* **27**, 93 (1997).

[8] K.R. Adam, A.J. Leong, L.F. Lindoy and B.J. McCool, *J. Chem. Soc., Dalton Trans.* 2537 (1987).

[9] D.E. Fenton, B.P. Murphy, A.J. Leong and L.F. Lindoy, *J. Chem. Soc., Dalton Trans.* 2543 (1987).

[10] C.A. Chang and V.O. Ochaya, *Inorg. Chem.* **25**, 355 (1986).

[11] C.A. Chang, P.H. Chang, V.K. Manchanda and S.P. Kasprzyk, *Inorg. Chem.* **27**, 3786 (1988).

[12] R.B. Lauffer, *Chem. Rev.* **87**, 901 (1987).

[13] K.R. Adam, G. Anderegg, L.F. Lindoy, H.C. Lip, M. McPartlin, J.H. Rea, R.J. Smith and P.A. Tasker, *J. Am. Chem. Soc.* **102**, 4645 (1980).

[14] *ASINT Software Reference Manual*, Siemens Energy & Automation Inc. (Madison, Wisconsin, 1994).

[15] *SMART Software Reference Manual*, Siemens Energy & Automation Inc. (Madison, Wisconsin, 1996).

[16] *SHELXTL 5 Reference Manual*, Siemens Energy & Automation Inc. (Madison, Wisconsin, 1994).

[17] D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2a, 2.3.1 (Kluwer Academic Publishers, Dordrecht, 1974).

[18] G. Anderegg, A. Ekstrom, L.F. Lindoy and R.J. Smith, *J. Am. Chem. Soc.* **102**, 2670 (1980).

[19] M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint and K. Pelin, *J. Chem. Soc., Dalton Trans.* 1342 (1980).

[20] A.W. Addison, T.N. Rao, J. Reedijk, J.V. Rijin and G.C. Verschoor, *J. Chem. Soc., Dalton Trans.* 1349 (1984).

[21] J.J. Drisoll and D.J. Kosman, *J. Am. Chem. Soc.* **109**, 1765 (1987).

[22] L.F. Lindoy, B.W. Skelton and A.H. White, *J. Am. Chem. Soc.* **105**, 4645 (1983).

[23] D.E. Fenton, B.P. Murphy, A.J. Leong and L.F. Lindoy, *J. Chem. Soc., Dalton Trans.* 2543 (1987).

[24] M. Lubben, R.H.A. Meetsma, K. Byma and B.L. Feringa, *Inorg. Chem.* **34**, 2217 (1995).

[25] S. Decurtins, H.W. Schmalle, P. Schneuwly and L.M. Zheng, *Inorg. Chem.* **34**, 5501 (1995).

[26] K.R. Adam, G. Anderegg and L.F. Lindoy, *Inorg. Chem.* **19**, 2956 (1980).

[27] K.R. Adam, K.P. Dancey, B.A. Harrison, L.F. Lindoy, M. McPartlin and P.A. Tasker, *J. Chem. Soc., Chem. Commun.* 1351 (1983).

[28] L.F. Lindoy, H.C. Lip, J.H. Rea and R.J. Smith, *Inorg. Chem.* **19**, 3360 (1980).

[29] K.R. Adam, A.J. Leong, L.F. Lindoy, B.J. McCool and P.A. Tasker, *J. Chem. Soc., Dalton Trans.* 2537 (1987).

[30] K.R. Adam, K.P. Dancey, A.J. Leong, L.F. Lindoy, M. McPartlin and P.A. Tasker, *J. Am. Chem. Soc.* **110**, 8471 (1987).