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Synthesis and characterization of a new series of 1D cobalt(II) complexes of pyridine derivative ligands with a single azido bridge and X-ray crystal structure of catena- $(\mu$ -N₃)[Co(4-methylpyridine)₄](PF₆)

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Abstract

A new series of polymeric cobalt(II) azido complex cations of the formula $[CoL_4(N_3)]PF_6-nH_2O$ (n=0 or 1), for L=some pyridine derivative ligands, have been prepared and characterized. Solid state electronic spectra suggest six-coordinated cobalt(II) in all complexes. IR spectral results reveal the existence of symmetrical azido ligand, except for complexes of L=3-Etpy and 4-Etpy(red) which contain asymmetrical azides, as well as PF_6^- counter ions in all complexes. X-ray crystal structure determination has shown the complex for L=4-methylpyridine to contain polymeric $[CoL_4(N_3)]^+$ cation and PF_6^- anions. In the cation, each cobalt(II) atom is coordinated by four nitrogen atoms from the pyridine ligands and two nitrogen atoms each from a μ -(1,3)-bridging azide giving rise to polymeric chains (1D) of six-coordinate Co(II) polyhedra. The azide ligand is symmetrical $[N_1-N_2=N_2-N_3=1.170(3) \text{ Å}]$ and linear within experimental error. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 1D Cobalt(II) azido complexes; Pyridine derivative complexes; Preparation of pyridine derivative complexes; Crystal structure; Spectra

1. Introduction

The azide ion N_3^- , is a versatile ligand which can bind atoms in a variable manner giving rise to terminal, end-on bridging and end-to-end bridging modes described somewhere else [1–8]. This versatility of the azide ligand not only enriches the stereochemistries of transition metal ions but also their spectroscopic and magnetic properties [9– 16].

Despite the fact that a substantial array of copper(II) azido complexes [17–23] of pyridine derivative ligands and very recently the corresponding manganese(II) azido complexes [24,25] have been synthesized, those of cobal-t(II) azide have received a little attention. Thus, in the early 1980s, some cobalt(II) azido complexes with pyridine derivative ligands of the general formula $CoL_2(N_3)_2$ have been reported [26,27] but none of them were determined by X-ray crystal diffraction. In a trial to synthesize polynuclear cobalt(II) complexes containing bridging azides of such pyridine ligands, we succeeded in the preparation of a new series of complexes of the general

formula $[CoL_4(N_3)]PF_6-nH_2O$ (n=0 or 1). This paper reports the synthesis and characterization of such a series of complexes along with the X-ray structure analysis of catena-(μ -N₃)[Co(4-methylpyridine)₄](PF₆), a typical member of this series.

2. Experimental

Pyridine derivative ligands were purchased from the Aldrich or BDH companies and other chemicals are of analytical grade quality.

Abbreviations for the pyridine ligands are given as a footnote under Table 1.

2.1. Preparation of complexes

2.1.1. $[Co(4-Mepy)_4(N_3)]PF_6$ (1)

This complex was prepared by mixing an aqueous solution of $Co(NO_3)_2-6H_2O$ (2.0 mmol) dissolved in 10 cm³ water and 4-Mepy (4.0 mmol) in ca. 10 cm³ ethanol, followed by KPF₆ (2.4 mmol, 3 cm³ water) and NaN₃(2.0 mmol) in ca. 3 cm³ water. The final clear solution mixture

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Table 1	
Analytical	data ^a

Complex	Color	Analytical: Found (required)				
		С	Н	Ν	Со	
$[Co(py)_4(N_3)]PF_6$	Violet crystals	42.3 (42.7)	3.8 (3.6)	17.8 (17.4)	10.0 (10.5)	
$[Co(4-Mepy)_4(N_3)]PF_6$	Violet-red crystals	46.1 (46.6)	4.8 (4.6)	15.5 (15.8)	9.3 (9.6)	
$[Co(4-Etpy)_4(N_3)]PF_6$	Pink powder	49.2 (49.8)	5.6 (5.4)	14.2 (14.5)	8.4 (8.7)	
$[Co(4-Etpy)_4(N_3)]PF_6^{b}$	Red crystals	49.6 (49.8)	5.3 (5.4)	14.6 (14.5)	8.3 (8.7)	
$[Co(3-Etpy)_4(N_3)]PF_6$	Violet powder	50.0 (49.8)	5.6 (5.4)	14.8 (14.5)	8.9 (8.7)	
$[Co(4-t-but-py)_4(N_3)]PF_6 \cdot H_2O$	Pink powder	53.2 (53.7)	6.7 (6.8)	12.5 (12.2)	7.6 (7.3)	
$[Co(4-Bzpy)_4(N_3)]PF_6 \cdot H_2O$	Violet	57.1 (57.8)	3.9 (3.8)	10.0 (9.8)	6.2 (5.9)	
$[Co(3-Bzpy)_4(N_3)]PF_6 \cdot H_2O$	Red	57.0 (57.8)	3.7 (3.8)	9.5 (9.8)	5.4 (5.9)	

^a Abbreviations: py, pyridine; Mepy, methylpyridine; Etpy, ethylpyridine; t-but-py, t-butylpyridine; Bzpy, benzoylpyridine.

^b Two types of crystals: red and deep violet both have similar analytical results.

was allowed to stand in an open beaker over several days until good quality violet crystals of the complex deposited.

2.1.2. $[Co(py)_4(N_3)]PF_6$

This complex was prepared by mixing $Co(NO_3)_2$ -6H₂O, pyridine, NaN₃ and KPF₆ in the molar ratio of 1:8:1:1.2, respectively, in ca. 30 cm³ aqueous–ethanol medium. The final clear solution mixture was allowed to stand over several days to produce the complex as red crystals along with a violet blue microcrystalline powder.

2.1.3. $[CoL_4(N_3)]PF_6 \cdot n(H_2O)$ (n=0 or 1) for L=3-,4-Bzpy, 4-t-butpy and 3-Etpy

These complexes were prepared in powder form just upon mixing the components as given in the procedure in Section 2.1.1. The filtrates in the case of 3-, and 4-Bzpy, however, deposit crystalline compounds of the 1:2 or 1:4 cobalt(II) azide complexes rather than the desired ones containing PF_6^- ions.

2.1.4. $[Co(4-Etpy)_4(N_3)]PF_6$ (pink form)

This complex was prepared according to the procedure in Section 2.1.3 which produces the complex as a pink powder. The filtrate deposits long pink crystals of the complex upon standing in open air over several days.

2.1.5. $[Co(4-Etpy)_4(N_3)]PF_6$ (red form)

This complex was prepared by mixing the components according to the procedure in Section 2.1.2. Filtration of the immediately formed precipitate and allowing the filtrate to stand over several days led to separation of two types of crystals; deep violet and red, of the same complex as shown by their elemental analysis and IR spectra.

The elemental analyses of the isolated complexes are collected in Table 1.

2.2. Physical measurements

The experimental procedures and instruments used for physical measurements were described previously [28].

2.3. X-ray crystallography

A modified STOE four-circle diffractometer was used. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 50 reflections in the θ range 8.8–14.4°. Data were collected at 298(2) K using graphite crystal-monochromatized MoK α radiation (λ =0.71069 Å) and the ω scan technique. The intensities were collected for Lorentz-polarization effects, for absorption and for intensity decay (intensities of three standard reflections dropped during data collection by 7%). The structure was solved by direct methods. Anisotropic displacement parameters were only applied to the nonhydrogen atoms in full-matrix least-squares refinement based on F^2 . The H atoms were included in the final refinement cycles on calculated positions. The disorder of PF_6^- counterions was taken into account by refining two split orientations with occupation factors of 0.676(14) and 0.324(14), respectively, and applying P-F distance restraints. The program DIFABS [29] and the SHELXTL/ PC [30] program package were used for computations. C₂₄H₂₈CoF₆N₇P, (FW=618.43), monoclinic, space group P2₁/C, *a*=10.406(3), *b*=11.183(3), *c*=24.630(8) Å, β= 90.51(3)°, *V*=2866(2) Å³, *Z*=4, μ(MoKα)=0.720 mm⁻¹, $D_{\rm calc}/D_{\rm obs} = 1.433/1.43(2) \text{ g cm}^{-3}$, crystal size= $0.50 \times$ 0.40×0.28 mm, 5048 reflections, 414 parameters, R= $0.0466, R_{int} = 0.0315.$

3. Results and discussion

3.1. Preparation of the complexes

The reactions between cobalt(II) ions, pyridine derivative ligands, azide and PF_6^- ions in aqueous–ethanol medium resulted in the isolation of cobalt(II) azido complexes given in Table 1. While mixing of cobalt(II) ion and pyridine derivative ligand, among other components, in the 1:2 molar ratio yielded $[CoL_4(N_3)]PF_6$ complexes with almost all given ligands, this ratio in case of pyridine itself led to the isolation of a 1:2 cobalt(II) azido complex rather than the desired complex containing PF_6^- anion. In order to obtain the pyridine complex, a large excess of pyridine (8 folds) with respect to cobalt (see Section 2) must be added. In the case of 4-Etpy, we isolated a form and two other forms; red and deep violet. Th spectra of these later forms could not be distingu from each other.

The isolated complexes, except those for L=3-, 4-Bzpy, are soluble in one or the other of the follow solvents, water, MeOH, EtOH, acetone, DMF and DM Complexes for L=3-, and 4-Bzpy are soluble only in 1 and DMSO with a change of their colors to blue. Aqu solutions of these complexes, except for L=3-, an Bzpy, behave as 1:1 electrolytes giving rise to 170 $\Omega \text{ cm mol}^{-1}$. This result suggests that they are is $[CoL_4(N_3)]^+ \cdot PF_6^-$ in aqueous solutions.

3.2. IR spectra

The IR spectra (Table 2) of the isolated comp suggest monodentate pyridine derivative ligands in complexes as indicated by the systematic shifts of vibrations related to pyridine nucleus and the appear of the carbonyl frequencies at the same positions in sp of both free and coordinated ligands. These spectra ex bands that can be readily assigned to the PF_6^- anions as follows; 550–560 s (ν_4), 740–745 w (ν_1) and 840 vs, br (ν_3) (all values in cm⁻¹). These results must meet the criteria for non-coordinated PF_6^- anions as described previously [31] and are consistent with the structure of complex (1). The spectra of all complexes, except those for L=3-Etpy and 4-Etpy (red form) show a single very strong band in the 2055–2100 cm⁻¹ range, due to the ν_{as} (N₃) mode. However, we could not locate any absorption band in the 1360–1270 cm⁻¹ range, due to the ν_s (N₃) mode in these spectra. The disappearance of the latter band is strong evidence of the symmetrical nature of the azido bridge not only in complex (1) as shown by the X-ray

Ta	ble 2			
IR	spectral	data	$(cm^{-1})^{a}$	

on 2)	bands at 2110 and 2077 cm ⁻¹ [ν_{as} (N ₃)] and a weak to
pink	medium band at 1344 cm ⁻¹ [ν_s (N ₃)] are observed. These
e IR	results suggest the existence of two azido ligands;
ished	symmetrical and asymmetrical μ -(1,3) bridges. Azide
	bridges of the type μ -(1,1) usually exhibit a strong band
and	around 1280 cm ^{-1} [17–23]. Thus we may assume dimeric
wing	structure for this complex containing di-µ-(1,3) azido
ASO.	ligands as well as octahedral cobalt(II) environment. In
DMF	case of the red form of the 4-Etpy complex, two bands are
ieous	observed at 2099 and 2055 cm ⁻¹ [ν_{as} (N ₃)] and two weak
d 4-	to medium bands at 1340 and 1289 cm ⁻¹ [ν_s (N ₃)]. These
-190	latter bands are not observed in the infrared spectrum of
onic:	the pink form, in addition to the 2085 cm ⁻¹ band [ν_s
	(N_3)]. As the spectrum of the pink form is very similar to
	that of 4-pic, therefore, this form has a polymeric cation
	$[Co(4-Etpy)_4(N_3)]^+$ with a $\mu(1,3)$ azide bridge. For the
	red form, the appearance of the 1289 cm^{-1} band suggests
lexes	that it contains two different azido ligands, $\mu(1,3)$ and
n all	$\mu(1,1)$ bridges, both, however, are asymmetric. We may
f the	assume that this red compound also is a dimer but contains
rance	simultaneous $\mu(1,3)$ and $\mu(1,1)$ bridging azides connecting
ectra	the same two cobalt atoms. Simultaneous $\mu(1,3)$ and
hibit	$\mu(1,1)$ azides linking the same two metal atoms were
[31]	previously observed in the structure of $[Cu(py)_2(N_3)_2]_n$
-845	[32].

Lattice water molecules are indicated by the appearance of a broad band of medium intensity centered around 3400 cm^{-1} in the infrared spectra of the respective complexes. In the far IR region we tentatively assigned [33,34] the bands in the 290–250 cm^{-1} and 240–210 cm^{-1} ranges to ν Co–N(azide) and ν Co–N(L) vibrations, respectively.

structure determination (described later), but also for the

other complexes. For the 3-Etpy complex, two very strong

3.3. Electronic spectra

The room temperature magnetic moments and the results

K spectral data (chi)						
Complex	Azide vibrat	tions		PF_6^- vibrations	vCo-N ₃	νCo–N
	$\nu_{as}N_3$	$\nu_{\rm s} {\rm N}_3$	δN_3			
$[Co(py)_4(N_3)]PF_6$	2101 vs	-	601 wm	844 vs, 750 m, 5595	290 wm	240 m
$[Co(4-Mepy)_4(N_3)]PF_6$	2075 vs	-	620 w 605 w	845 vs,br, 745 wm, 550 m	275 wm	235 w
$[Co(4-Etpy)_4(N_3)]PF_6^{b}$	2085 vs	_	614 w	844 vs,br, 740 w, 558 s	278 w	228 wm
$[Co(4-Etpy)_4(N_3)]PF_6^{c}$	2099 vs	1340 wm	660 w	846 vs, 740 w, 557 s	282 wm	222 wm
	2055 vs	1289 m	623 w		275 sh	
$[Co(4-t-but-py)_4(N_3)]PF_6 \cdot H_2O$	2089 vs	_	610 w	842 vs, 724 w, 558 m	285 w	232 w
$[Co(4-Bzpy)_4(N_3)]PF_6 \cdot H_2O$	2073 vs	-		840 s, 742 wm, 558 m	272 wm	225 wm
$[Co(3-Bzpy)_4(N_3)]PF_6 \cdot H_2O$	2056 vs	_	610 w	845 vs, 743 wm, 558 m	265 wm	233 wm
$[Co(3-Etpy)_4(N_3)]PF_6$	2101 vs	1344 wm	614 w	844 vs,br, 757 s	280 w	229 wm
	2077 vs				260 w	

^a v, very; s, strong; m, medium; w, weak; br, broad.

^b Pink form.

^c Red form.

of electronic spectral measurements of the isolated complexes are collected in Table 4. The magnetic moments of 4.8–5.1 B.M. given for those complexes fall in the range 4.8–5.6 B.M. expected [35] for high-spin six-coordinate cobalt(II) complexes and above the ranges associated with tetrahedral or high-spin five-coordinate cobalt(II). These values, however, do not indicate whether the complexes display the metal–metal interaction expected in complexes containing μ -(1,3) bridging azides. In fact, similar nickel(II) complexes with a single μ -(1,3) azide bridge have been found to exhibit strong antiferromagnetic coupling between nickel(II) ions through the N₃⁻ bridge [36,37]. Nevertheless, a detailed magnetic susceptibility at variable temperature should be done in order to obtain a better understanding of this effect.

The electronic spectra (Table 3) of solid complexes are typical of cobalt(II) in a weak octahedral field and show the ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$, transition as a band of moderate intensity around 19 300 cm⁻¹ with a shoulder at high frequency and sometimes another shoulder at lower frequency. For the series of complexes derived from 4-substituted pyridine ligands the position of the main band is shifted to lower energy in the order 4-t-but-py>py>4-Etpy>4-Mepy>4-Bzpy. In methanol, the main band is shifted to lower wave numbers or two separate bands are observed.

3.4. Structure of $[Co(4-Mepy)_4(N_3)](PF_6)$ (1)

The principal structural features of the complex (1) are illustrated in Figs. 1 and 2, and selected bond distances and angles are given in Table 4. The structure of 1 consists of 1D cobalt-azido chains, isolated by PF_6^- anions, which are found in the interchain space. In the chain structure each cobalt(II) atom is coordinated by four nitrogen atoms from the four pyridine ligands and two azido ligands in an octahedral trans arrangement. The four N atoms of the

Table 3					
Electronic	spectral	data	and	magnetic	moments



Fig. 1. [Co(4-methylpyridine)₄(N₃)] PF₆, 1: Molecular geometry and atom labeling scheme. For clarity only disordered PF₆⁻ counter ion with occupancy of 0.676(14) is given (atoms represented as spheres with arbitrary size).

pyridine ligands are in the same plane (maximum deviation from plane=0.025(1) Å); the coordination of the $\mu(1,3)$ azido bridge is almost symmetrical; the two Co–N–N angles are 135.3(3) and 133.0(3)°, respectively, and the torsion angle Co–NNN–Co is –99.2(3) Å. The four Co– N(L) distances are variable from 2.135(3) to 2.201(3) Å, whereas the Co–N(N₃) bond lengths are 2.120(3) and 2.135(3) Å. The azido ligand itself is symmetrical [N₁– N₂=N₂–N₃=1.170(4) Å] and linear [<NNN=177(4) °] within the experimental error.

A single $\mu(1,3)$ azido bridge has previously been found in the cation in $[Ni_2(Me_4Cyclam)_2(N_3)_3]I$ [38,39]. Furthermore, X-ray analyses of Mn(acac)₂N₃ has established

Complex	Solvent	λ_{\max} (cm ⁻¹)	$\mu_{\rm eff}$ (B.M.) ^a
$[Co(py)_4(N_3)]PF_6$	NM^{b}	21739 sh, 19607, 17857 sh	4.82
	MeOH	21186, 18348	
$[Co(4-Mepy)_4(N_3)]PF_6$	NM	20833 sh, 18975, 18181 sh	4.80
$[Co(4-Etpy)_4(N_3)]PF_6^{c}$	NM	26315, 19607	4.90
	MeOH	20833	
$[Co(4-Etpy)_4(N_3)]PF_6^d$	NM	21700 sh, 19047	4.84
$[Co(4-t-but-py)_4(N_3)]PF_6 \cdot H_2O$	NM	19880, 18181 sh, 16501	5.10
	MeOH	16500	
$[Co(4-Bzpy)_4(N_3)]PF_6 \cdot H_2O$	NM	20000 sh, 18867, 17857 sh	5.00
$[Co(3-Bzpy)_4(N_3)]PF_6 \cdot H_2O$	NM	18510	4.96
$[Co(3-Etpy)_4(N_3)]PF_6$	NM	19417, 17857 sh	4.80
	MeOH	16666	

^a Measured at room temperature.

^b NM, Nujol mull.

° Pink form.

^d Red form.



Fig. 2. $[Co(4-methylpyridine)_4(N_3)] PF_6$, 1: Packing plot with chains of polyhedra oriented along the *b*-axis of unit cell.

the presence of single $\mu(1,3)$ azide bridging which links adjacent metal atoms to form polymeric chains of sixcoordinate Mn(III) polyhedra [36]. The structure of the present complex resembles that of catena- $\mu(N_3)$ -[Ni(Cyclam)]ClO₄·H₂O (Cyclam=1,4,8,11-tetraazocyclotetradecane) (2) [33] which features six-coordinate Ni(II), trans arrangement, 1D nickel azide chains and ClO₄⁻ anions. Complex (2) differs in the asymmetric arrangement of the azido bridge; the two Ni–N–N angles are 140.7(3) and 128.2(3)°, the azide ligand itself is asymmetric (N₁–N₂=1.178(5), N₂–N₃=1.138(5) Å), as well as the bond length of the two Ni–N(azide) distances

Table 4								
Selected	bond	lengths	(Å)	and	angles	(°)	for	$(1)^{i}$

Co(1)–N(13a)	2.130(3)	Co(1)-N(11)	2.137(3)
Co(1)-N(4)	2.158(3)	Co(1) - N(2)	2.194(3)
Co(1) - N(1)	2.200(3)	Co(1)–N(3)	2.201(3)
N(11)–N(12)	1.168(3)	N(12)-N(13)	1.170(3)
N(13a)-Co(1)-N(11)	176.01(11)	N(13a)-Co(1)-N(4)	93.24(11)
N(11)-Co(1)-N(4)	90.37(11)	N(13a)-Co(1)-N(2)	91.82(10)
N(11)-Co(1)-N(2)	90.16(10)	N(4)-Co(1)-N(2)	85.46(10)
N(13a)-Co(1)-N(1)	87.94(10)	N(11)-Co(1)-N(1)	90.78(10)
N(4)-Co(1)-N(1)	83.52(10)	N(2)-Co(1)-N(3)	168.95(10)
N(13a)-Co(1)-N(3)	89.90(10)	N(11)-Co(1)-N(3)	86.45(10)
N(4)-Co(1)-N(3)	167.59(10)	N(2)-Co(1)-N(3)	95.76(10)
N(1)-Co(1)-N(3)	95.28(10)	N(12)-N(11)-Co(1)	135.4(2)
N(11)-N(12)-N(13)	177.5(3)	N(11)-N(12)-N(13)	132.9(2)

^a Symmetry code: (a) -x+1, y+1/2, -z+3/2; (b) -x+1, y-1/2, -z+3/2.



Fig. 3. Thermal decomposition of $[Co(4-methylpyridine)_4(N_3)]$ PF₆.

are longer (2.165 and 2.172 Å) than the four Ni–N(Cyclam) distances (2.059 to 2.073 Å).

3.5. Thermal analysis of (1)

Fig. 3 represents the TGA and DTA curves for the thermal decomposition of complex (1). It is clear that the complex is stable till ca. 120°C at which it starts decomposition which takes place in the 120-260°C range with an experimental loss of weight of 72.8%. This value correspond to a loss of four 4-pic molecules, an azide and two F atoms (Calcd.: 73.4%). The IR spectrum at 250°C shows that the residue contains traces of 4-pic but no azide at all. It also shows a little change in the appearance and position (not intensities) of the bands at 840 and 558 cm^{-1} and a disappearance of the 720 cm⁻¹ (weak) band, all of them are related to the PF₆ group. The former bands remain and appear in the spectrum of the residue at 400°C. This step does not reflect a simple one-stage process and the DTA curve shows a weak endotherm ($T_{\rm max} = 170^{\circ}$ C and $\Delta H = -$ 59.7 kJ mol⁻¹), followed by a narrow exotherm at $T_{\text{max}} =$ 202.4°C (ΔH =154.6 kJ mol⁻¹) and then two successive endotherms with $T_{\text{max}} = 231.8$ and 249°C and $\Delta H = -18.5$ kJ mol⁻¹ and -12.3 kJ mol⁻¹, respectively.

Supplementary data

Further details of the crystal structure investigation are available on request from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 7EZ, UK, on request, quoting the deposition number CCDC 111534.

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References

- N.A. Baily, D.E. Fenton, C.H. Mclean, Inorg. Chim. Acta 179 (1991) 1.
- [2] P. Chauhuri, M. Guttman, D. Ventur, K. Wieghart, B. Nuber, J.J.J. Weiss, J. Chem. Soc., Chem. Commun. (1985) 1618.
- [3] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, Inorg. Chem. 32 (1993) 3557.
- [4] J. Ribas, M. Monfort, B.K. Ghosh, R. Cortes, X. Solans, M. Font-Brdia, Inorg. Chem. 35 (1996) 864.
- [5] E.G. Arriortue, M.I. Corte's, A.R. Lezama, L. Rojo, X. Solans, Inorg. Chim. Acta 174 (1990) 263.
- [6] A. Escuer, R. Vicente, J. Ribas, J. Magn. Magn. Mater 110 (1992) 181.
- [7] M.A.S. Goher, T.C.W. Mak, Inorg. Chim. Acta 99 (1985) 223.
- [8] Z. Dori, R.F. Ziolo, Chem. Rev. 73 (1973) 247.
- [9] L. Casella, M. Gullotti, G. Pallance, M. Buga, Inorg. Chem. 30 (1991) 221.
- [10] J.E. Pate, P.K. Ross, T.J. Thaman, C.A. Reed, K.D. Karlin, T.N. Sorell, E.I. Solomon, J. Am. Chem. Soc. 111 (1988) 5198.
- [11] J. Peisach, W.E. Blumberg, Arch. Biochem. Biophys. 165 (1974) 691.
- [12] K.H. Falk, E. Ivanova, B. Roos, T. Vanngard, Inorg. Chem. 9 (1970) 556.
- [13] H. Okawa, D.H. Bush, Inorg. Chem. 18 (1979) 1555.
- [14] Reedjik, Transition Met. Chem. 6 (1981) 195.
- [15] O. Kahn, M.L. Boilor, in: K.D. Karlin, J. Zubeta (Eds.), Biochemical and Inorganic Aspects of Copper Coordination Chemistry, Vol. 2, Adenine Press, New York, 1983.
- [16] M.-F. Charlot, O. Kahn, M. Chaillet, Ch. Larrieu, J. Am. Chem. Soc. 108 (1986) 2574.

- [17] T.C.W. Mak, M.A.S. Goher, Inorg. Chem. Acta 115 (1986) 17.
- [18] M.A.S. Goher, R.-J. Wong, T.C.W. Mak, J. Mol. Strut. 243 (1991) 179.
- [19] F.A. Mautner, M.A.S. Goher, Polyhedron 11 (1992) 2537.
- [20] F.A. Mautner, M.A.S. Goher, Polyhedron 12 (1993) 2823.
- [21] F.A. Mautner, M.A.S. Goher, Polyhedron 13 (1994) 2141.
- [22] M.A.S. Goher, F.A. Mautner, Polyhedron 14 (1995) 1751.
- [23] M.A.S. Goher, F.A. Mautner, Polyhedron 15 (1996) 5.
- [24] A. Escuer, R. Vicente, M.A.S. Goher, F.A. Mautner, Inorg. Chem. 36 (1997) 3440, and references therein.
- [25] M.A.S. Goher, N.A. Al-Salam, F.A. Mautner, J. Coord. Chem. 44 (1998) 119.
- [26] M.A.S. Goher, A.A. Hassanein, G.H. El-Subrutti, Bull. Soc. Chim. Fr. (1982) I-221.
- [27] M.A.S. Goher, A.A. Hassanein, S.M. Soliman, Bull. Soc. Chim. Fr. (1982) I-449.
- [28] M.A.S. Goher, T.C.W. Mak, Polyhedron, in press.
- [29] N. Walker, D. Stuart, Acta Crystallogr., Sect. A 39 (1983) 158.
- [30] SHELXTL/PC v. 5.03, Siemens Analytical Automation, Madison, WI (1995).
- [31] F. Wagner, M.T. Mocella, M.J. D'Aneillo, A.H.J. Wang, E.K. Barafield, J. Am. Chem. Soc. 96 (1974) 2625.
- [32] V.W. Day, B.R. Stults, E.L. Tasset, R.O. Day, R.S. Marianelli, J. Am. Chem. Soc. 96 (1974) 2650.
- [33] A. Escuer, R. Vicente, J. Ribas, M.S. El-Fallah, X. Solans, Inorg. Chem. 32 (1993) 1033.
- [34] R.M. Morrison, R.C. Thompson, Can. J. Chem. 56 (1978) 985.
- [35] B.N. Figgis, J. Lewis, Progr. Inorg. Chem. 4 (1964) 37.
- [36] R.J.H. Clark, C.S. Williams, Inorg. Chem. 4 (1965) 350.
- [37] C.W. Frank, L.B. Rogers, Inorg. Chem. 5 (1966) 615.
- [38] B.N. Figgis, J. Lewis, Prog. Inorg. Chem. 6 (1964) 37.
- [39] C.G. Pierpont, D.N. Hendrickson, D.M. Duggan, F. Wagner, E.K. Barefield, Inorg. Chem. 14 (1975) 604.