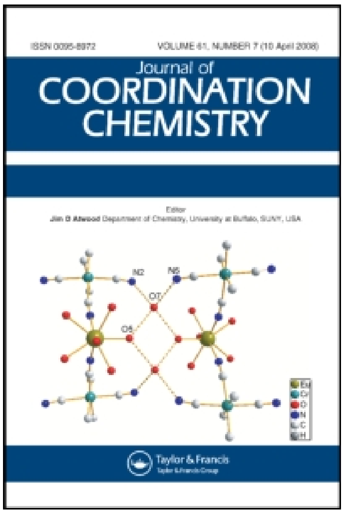

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MIXED DINUCLEAR Co(II) COMPLEXES WITH *N,N',N'',N'''* -TETRAKIS-(2-PYRIDYLMETHYL)-l, 4, 8, 11-TETRAAZACYCLOTETRADECANE AND α - AND β-AMINOCARBOXYLATO LIGANDS

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MIXED DINUCLEAR Co(II) COMPLEXES WITH *N,N′,N″,N‴*-TETRAKIS-(2-PYRIDYLMETHYL)-1,4,8,11-TETRAAZACYCLOTETRADECANE AND α- AND β-AMINOCARBOXYLATO LIGANDS

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Four new mixed complexes of Co(II) with *N,N′,N″,N‴*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) and bridged α- or β-aminocarboxylato ligands of general formula $[Co_2(Y)tpmc](ClO_4)_3 \cdot zH_2O$ where Y = glycinato, *S*-alaninato, *S*-aminobutyrato, β-aminobutyrato ion, and $z = 0$, 0.5 or 1 were isolated. The complexes were characterised by elemental analysis, electronic and IR spectroscopy, magnetic measurements and cyclic voltammetry. A structure with μ-O,O′-coordination of the aminocarboxylato ligand, and *exo* coordination of Co(II) ions and tpmc is proposed. The complexes exhibit different electrochemical activities; glycinato and *S*-alaninato complexes are electrochemically active, whereas *S*-aminobutyrato and β-aminobutyrato complexes are electrochemically inactive under the given conditions.

Keywords: Dinuclear; Co(II) complexes; octaaza pendant arm macrocycle; aminocarboxylates; cyclic voltammetry

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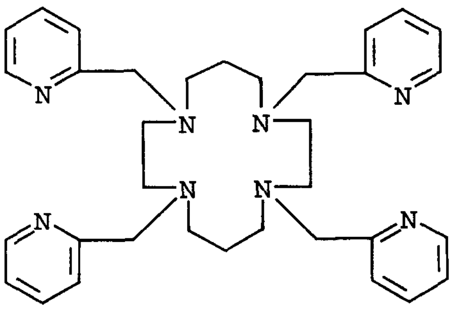
INTRODUCTION

The octaaza pendant arm macrocyclic ligand *N*,*N*′,*N*″,*N*‴-tetrakis-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc, **1**) has been found to form dinuclear complexes with two metal ions coordinated outside the macrocyclic ring (*exo* coordination). Additional ligands can act as a bridge between the two metal ions.[1–4]

Dinuclear Co(II) complexes with tpmc and OH^-, CO_3^{2-}, α-aibu⁻ or β-aibu⁻ as the bridge ligand[a] have been described.[3,4] The complexes are stable against oxidation by air while the oxidation of carbonato[3] and α-aminoisobutyrato complex[4] by hydrogen peroxide yielded mixed-valence Co(II)/Co(III) complexes. In these complexes tpmc adopts a boat conformation with an *exo* coordination mode. At the same time μ-O,O′-coordination of aminocarboxylato ligands was proposed.[4]



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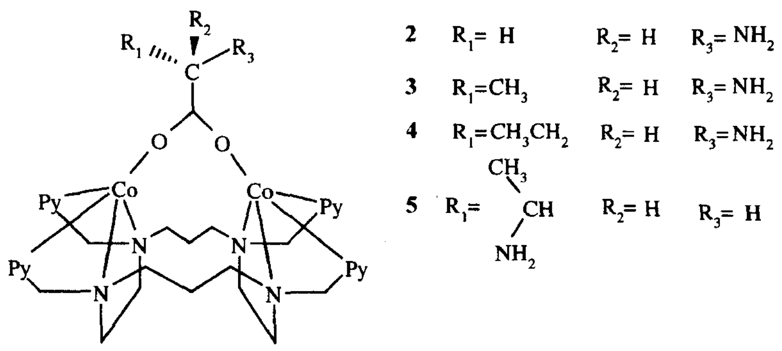
SCHEME 1



2	$R_1 = H$	$R_2 = H$	$R_3 = NH_2$
3	$R_1 = CH_3$	$R_2 = H$	$R_3 = NH_2$
4	$R_1 = CH_3CH_2$	$R_2 = H$	$R_3 = NH_2$
5	$R_1 = CH(CH_3)NH_2$	$R_2 = H$	$R_3 = H$

SCHEME 2

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[a] α-aibu⁻ = α-aminoisobutyrato-; β-aibu⁻ = β-aminoisobutyrato-ion.

After further investigation, four new complexes containing in the bridge gly, S-ala$^-$, S-abu$^-$ and β-abu$^-$ were obtained.[b] This paper compares them to corresponding complexes with branched chain aminocarboxylato ligands described earlier.

EXPERIMENTAL

Safety note. Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should not be heated in the solid state.

Syntheses

The macrocyclic ligand tpmc was prepared by a procedure described in the literature.[1] All other chemicals were obtained commercially and used without further purification.

$[Co_2(Y)tpmc](ClO_4)_3 \cdot zH_2O$ (Y = gly$^-$, S-ala$^-$, S-abu$^-$, β-abu$^-$; z = 0, 0.5, 1)

General procedure To a suspension of 0.142 g (0.25 mmol) of tpmc in 5 cm^3 of CH_3CN, a solution containing 0.176 g (0.50 mmol) of $Co(ClO_4)_2 \cdot 6H_2O$ in 4 cm^3 water was added. The mixture was stirred for a short time and then a neutralized (pH = 8) solution containing 0.25 mmol of amino acid in minimum amount of water was added. The reaction mixture, which had an intense purple colour was continuously stirred and heated at 60°C on a water bath for 2 h. On cooling to room temperature, a crude product containing as impurity the previously described violet complex $[Co_2(OH)$-tpmc$](ClO_4)_3$[3] separated. Recrystallization from $CH_3CN:H_2O$ (5:1, v/v) yields pure product as purple crystals.

$[Co_2(gly)tpmc](ClO_4)_3$ (**2**): Yield 0.103 g (39%). *Anal.*: calcd. for $C_{36}H_{48}N_9Cl_3O_{14}Co_2$ (%): C, 40.98; H, 4.59; N, 11.95. Found: C, 40.93; H, 4.33; N, 11.80.

$[Co_2(S\text{-}ala)tpmc](ClO_4)_3 \cdot H_2O$ (**3**): Yield 0.180 g (66%). *Anal.*: calcd. for $C_{37}H_{52}N_9Cl_3O_{15}Co_2$ (%): C, 40.89; H, 4.82; N, 11.60. Found: C, 41.16; H, 4.89; N, 11.72.

$[Co_2(S\text{-}abu)tpmc](ClO_4)_3 \cdot H_2O$ (**4**): Yield 0.185 g (67%). *Anal.*: calcd. for $C_{38}H_{54}N_9Cl_3O_{15}Co_2$ (%): C, 41.44; H, 4.94; N, 11.45. Found: C, 41.76; H, 4.68; N, 11.40.

$[Co_2(\beta\text{-}abu)tpmc](ClO_4)_3 \cdot 0.5H_2O$ (**5**): Yield 0.246 g (45%). The complex was obtained by a similar procedure to that described above, except that the

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[b] gly$^-$ = glycinato-; S-ala$^-$ = S-alaninato-; S-abu$^-$ = S-aminobutyrato-; β-abu$^-$ = β-aminobutyrato-ion.

solvent was $CH_3CN:H_2O$ (10 : 1, v/v), and the reaction mixture was heated at 90°C on a water bath for 2 h. The crude product was recrystallized from CH_3CN. *Anal.*: calcd. for $C_{38}H_{53}N_9Cl_3O_{14.5}Co_2$ (%): C, 41.79; H, 4.89; N, 11.54. Found: C, 41.89; H, 4.50; N, 11.12.

Measurements

Electronic absorption spectra in CH_3CN solutions were recorded on a GBC-UV/VIS 911A spectrophotometer. Reflectance spectra were recorded on a CARY 17D spectrophotometer using $MgCO_3$ as standard. IR spectra were run on a Perkin-Elmer 31725X FTIR spectrophotometer using the KBr disc technique. Magnetic susceptibility measurements were made at room temperature (25 ± 2°C) using an MSB-MKI balance (Sherwood Scientific Ltd., Cambridge, England). Data were corrected for diamagnetic susceptibilities. Optical rotation data, for complexes **3** and **4**, were obtained on a Perkin-Elmer 141 MC polarimeter at $\lambda = 589\,\text{nm}$. Electrochemical experiments were performed in a standard three-electrode cell [Pt as a counter electrode, saturated calomel electrode (SCE) as reference and glassy-carbon (GC, Tacusel) as test electrode]. The surface of the electrode obtained was checked by cyclic voltammetry (CV) in $100\,\text{cm}^3$ of aqueous NaOH $(0.1\,\text{mol}\,\text{dm}^{-3})$: CCHCN (70 : 30, v/v). Then it was immersed in a solution of the examined complexes $(10^{-4}\,\text{mol}\,\text{dm}^{-3})$ for 30 min, or the complexes were added directly into the cell. CV was performed at a sweep rate of $100\,\text{mV}\,\text{s}^{-1}$ whereas potential ranged from -0.6 V to $+0.4$ V *vs* SCE. Preparation of the GC electrode, other conditions and electronic equipment were the same as described earlier.[5]

RESULTS AND DISCUSSION

In a previous paper dinuclear complexes of Co(II) and tpmc, containing bridged branched chain amino acids α-aibu$^-$ and β-aibu$^-$, as well as the mixed-valence Co(II)/Co(III) complex,[4] were described. The μ-O,O′-coordination mode of the aminocarboxylato ligand was proposed. In this paper four new mixed Co(II) complexes, containing α- and β-aminocarboxylato ligands with linear side chain: gly$^-$, *S*-ala$^-$, *S*-abu$^-$ or β-abu$^-$, are described. CV indicates different electrochemical activities of the complexes.

The complexes were prepared by direct synthesis. Elemental analyses correspond with a dinuclear structure in agreement with earlier results.[4] Electronic absorption and magnetic data for the complexes are listed in Table I.

TABLE I Electronic spectra and μ_{eff} per Co atom at room temperature (BM/Co)

Complex	λ/nm (ε/dm^3 cm^{-1} mol^{-1})						μ_{eff}
	Acetonitrile solution			*Reflectance*			
2	458(80)	511(96)	548(79)sh*	452	508	560sh	4.70
3	459(60)	512(75)	551(58)sh	452	508	560sh	4.62
4	454(67)	510(79)	548(64)sh	447	512	568sh	4.72
5	467(71)	490(60)sh	544(75)	454	498sh	528	3.96
$[Co_2(\alpha\text{-aibu})tpmc](ClO_4)_3$[†]	456(99)	514(115)	559(96)sh				4.10
$[Co_2(\beta\text{-aibu})tpmc](ClO_4)_3 \cdot H_2O$[†]	468(86)	513(74)	544(76)				4.55

*Data from the literature;[8] [†]sh = shoulder.

Electronic spectra correspond to high-spin, five coordinate Co(II) complexes.[6,7] The complexes obtained exhibit similar spectra, which indicates a similar coordination mode. Absorption maxima of the reflectance spectra (Table I) exhibit a close correlation with the values recorded in solution, and indicates that the complexes are stable in solution. The molecular rotation values $[M]_{589}^{20}$ of complexes containing optically active acids *S*-alanine and *S*-aminobutyric acids, are +167.7° and +125.5°. The low values are probably the result of vicinal effect alone.[8]

Magnetic measurements are in agreement with dinuclear high-spin Co(II) complexes.[2,4,9–13] At room temperature, μ_{eff} values (Table I) are higher than $\mu_{\mathrm{s.o.}}$ value (3.88 BM/Co) and are in the expected range 3.96–4.72 BM/Co for paramagnetic high-spin Co(II) complexes. In the case of complex **5**, the relatively low value of μ_{eff} is perhaps a consequence of the presence of antiferromagnetic interactions.[2,9–11]

The significant regions in the IR spectra of all complexes (Table II) are very similar and only the following observations are of interest. A very broad band at 3590–3220 (s) belonging to ν(O–H) from crystalline water and ν(N–H) is observed. Skeletal pyridine vibrations are seen at 1600 (s); $\nu_{\mathrm{as}}(\mathrm{COO^-})$ is in the range 1580–1574 (s) and $\nu_{\mathrm{s}}(\mathrm{COO^-})$ in the range 1390–1350 (s); $\nu(\mathrm{ClO_4^-})$ at 1100 (s, broad) and $\delta(\mathrm{ClO_4^-})$ at 620 cm^{-1} (m, sharp),[8] where s and m refer to strong and medium intensities, respectively, are prominent.

A comparison of IR spectra of complexes with those of alkali salts of the corresponding amino acids helps to distinguish the coordination mode of the aminocarboxylato ligand.[4,14–17] The $\Delta\nu(\mathrm{COO^-})$ values listed in Table II, where $\Delta\nu = \nu_{\mathrm{as}} - \nu_{\mathrm{s}}$, are somewhat greater for all complexes than in the case of alkali salts. At the same time, values of ν_{as} and ν_{s} of the complexes are somewhat lower in relation to alkaline salts of corresponding amino acids. Both observations suggest that the aminocarboxylato ligands, as in the case

TABLE II Characteristic ν_{as}, ν_{sym} and $\Delta\nu$ values of aminoacid salts and complexes

Compound	ν_{as}	ν_{sym}	$\Delta\nu$
Na-gly	1595s	1399s	196
2	1580m	1365m	215
Na-*S*-ala	1595s	1406s	189
3	1575m	1350w	225
K-*S*-abu	1587s	1408s	179
4	1575m	1390m	185
K-β-abu	1576s	1402m	174
5	1574s	1377m	197
K-α-aibu*	1577vs	1416vs	161
$[Co_2(\alpha\text{-aibu})tpmc](ClO_4)_3$*	1555s	1361w	194
K-β-aibu*	1584vs	1408m	176
$[Co_2(\beta\text{-aibu})tpmc](ClO_4)_3 \cdot H_2O$*	1543m	1355m	188

*Data from the literature.[5]
vs = very strong; s = strong; m = medium; w = weak.

TABLE III Values of anodic and cathodic peak potentials of complexes **2** and **3**

Complex	*E*(*V vs SCE*)			
	E_{a1}*	E_{a2}	E_{c1}†	E_{c2}
$[Co_2(gly)tpmc](ClO_4)_3$	0.10	0.40	0.00	0.30
$[Co_2(S\text{-ala})tpmc](ClO_4)_3 \cdot H_2O$	0.05	0.35	0.00	0.30

*E_a = anodic potential; †E_c = cathodic potential.

of α-aibu$^-$ and β-aibu$^-$ complexes,[4] are coordinated through the COO$^-$ group (Scheme 2) forming a O,O′-bridge between metal ions.[4,17]

The complexes exhibit two types of electrochemical behaviour. The first is characteristic of complexes **2** and **3**. Reversible charge transfer at the electrode occurs twice, which is expressed by two oxido-reduction peaks in the anodic and cathodic directions. The values of peaks of electrochemical potentials of **2** and **3** are shown in Table III, and their voltammograms in Figure 1.

This is the first case of dinuclear Co(II) complexes having CN 5 with octaaza pendant arm ligands derived from cyclam, undergoing a two-step reversible electrochemical oxidation. Among these complexes, those that are electrochemically active exhibit either two irreversible oxidation peaks[10] or one reversible and one irreversible oxidation.[3] Carbonato Co(II) complexes with pendant ligands derived from cyclam are the only ones which exhibit two reversible oxidation peaks.[3,10]

Anodic and cathodic peaks of complex **2** (Figure 1(a)) look reversible, and of complex **3** (Figure 1(b)) exhibit two charge transfer processes. The capacitive current in the cyclic voltammograms (Figure 1(a) and (b))

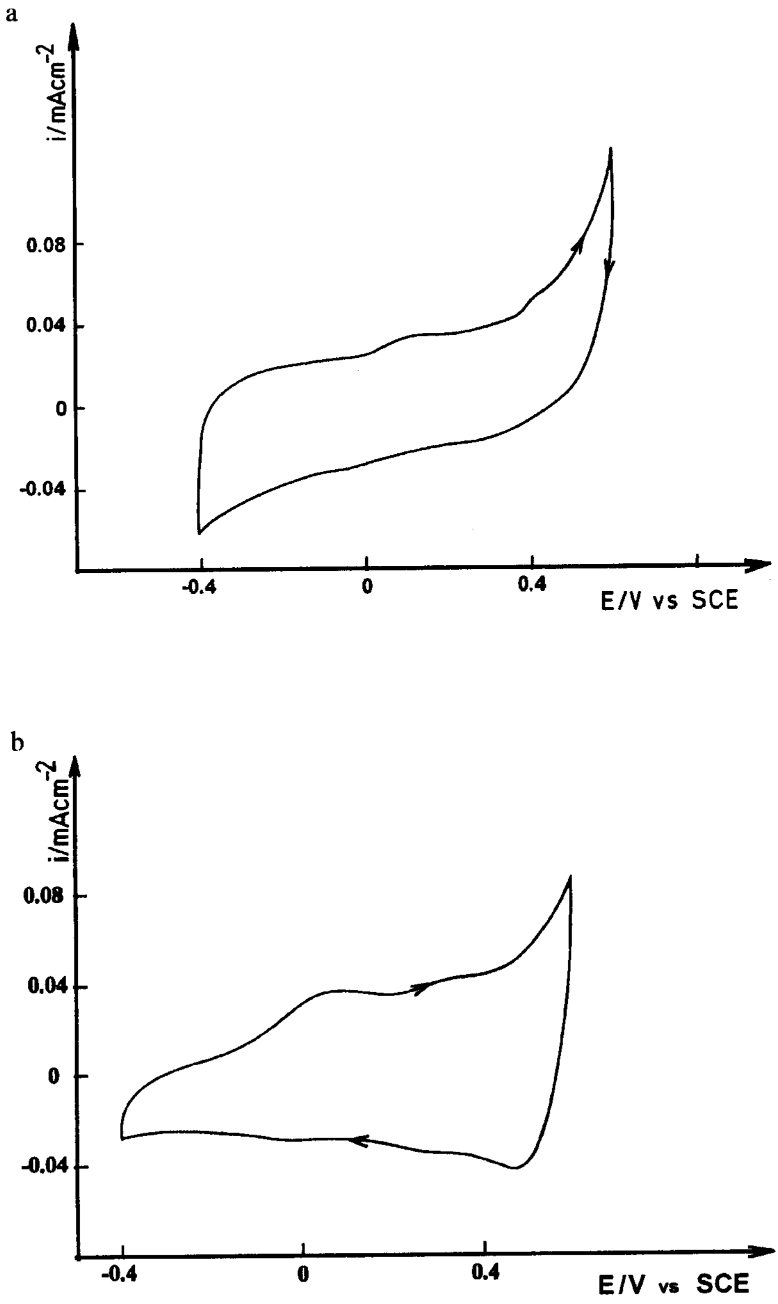

FIGURE 1(a) and (b)

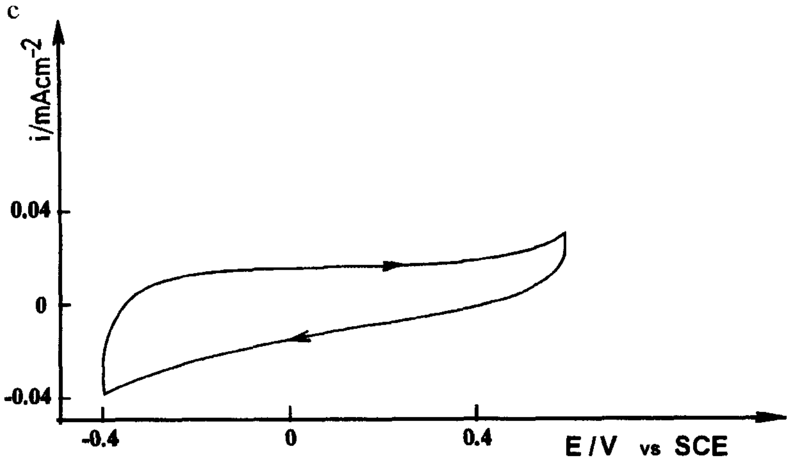

FIGURE 1(c)

FIGURE 1 CV of a stationary GC electrode in 100 cm^3 NaOH (0.1 mol dm^{-3}) : CH_3CN (70 : 30, v/v) in the presence of (a): complex **2**; (b): complex **3**; (c): complexes **4** or **5**, as well as the GC electrode alone; sweep rate = 100 mV s^{-1}.

is very large. The origin of this capacitive current is not clear, but it is not consequence of the trace impurities. We suppose that first anodic peak corresponds to $Co^{II}Co^{II} \rightarrow Co^{II}Co^{III}$ and the second to $Co^{II}Co^{III} \rightarrow Co^{III}Co^{III}$ oxidation.[3] Both complexes are destroyed at 0.6 V potential, presumably due to anodic oxidation of ligands.

The other kind of behaviour is exhibited by complexes **4** and **5**. They are under the given experimental conditions electrochemically inactive like the previously described complex with β-aibu$^-$.[4] Voltammograms are identical as those of the GC electrode (Figure 1(c)). Extension of the potential limit toward more negative values leads neither to complex adsorption not to electron transfer at the electrode.

Electrochemical behaviour coincides significantly with $\Delta\nu$ values. Complex **3**, having the highest $\Delta\nu$ value, exhibits the greater electrochemical activity, and complex **2** having $\Delta\nu$ value next to highest exhibits somewhat lower activity. Previously described complexes with α-aibu$^-$ exhibit a third type of electrochemical behaviour.[4] It is adsorbed on the surface of electrode, but there is no charge transfer. We assume that the differences in the electrochemical behaviour of the complexes are a consequence of differences between their conformations caused by the change of bridging ligand.

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References

[1] N.W. Alcock, K.P. Balakrishnan and P. Moore, *J. Chem. Soc., Dalton Trans.* 1743 (1986).
[2] I. Murase, M. Mikuriya, H. Sonoda, Y. Fukuda and S. Kida, *J. Chem. Soc., Dalton Trans.* 953 (1986).
[3] H. Harada, M. Kodera, G. Vučković, N. Matsumoto and S. Kida, *Inorg. Chem.* **30**, 1190 (1991).
[4] G. Vučković, D. Opsenica, S.P. Sovilj, D. Poleti and M. Avramov-Ivić, *J. Coord. Chem.* **41**, 231 (1998), and references therein.
[5] S.P. Sovilj, G. Vučković, K. Babić, N. Matsumoto, M. Avramov-Ivić and V.M. Jovanović, *J. Coord. Chem.* **31**, 167 (1994).
[6] B.N. Figgis, *Introduction to Ligand Fields* (Interscience, New York, 1967), p. 223.
[7] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn. (Elsevier, Amsterdam, 1984), pp. 480–505.
[8] Y. Shimura, *Bull. Chem. Soc. Jpn.* **31**, 315 (1958).
[9] M. Mikuriya, S. Kida, T. Kohzuma and I. Murase, *Bull. Chem. Soc. Jpn.* **61**, 2666 (1988).
[10] I. Murase, G. Vučković, M. Kodera, H. Harada, N. Matsumoto and S. Kida, *Inorg. Chem.* **30**, 728 (1991).
[11] Z. Dori and H.B. Gray, *Inorg. Chem.* **7**, 889 (1968).
[12] J. Reedijk, J.C. Jansen, H. van Koningsveld and C.G. van Kralingen, *Inorg. Chem.* **17**, 1990 (1978).
[13] D.L. Kepert, E.S. Kucharski and A.H. White, *J. Chem. Soc., Dalton Trans.* 1932 (1980).
[14] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Ed. (J. Wiley and Sons, New York, 1978).
[15] A.J. Saraceno, I. Nakagava, S. Mizusima, C. Curron and J.V. Quagliano, *J. Am. Chem. Soc.* **80**, 5018 (1958).
[16] C.A. McAuliffe, J.V. Quagliano and L.M. Vallarino, *Inorg. Chem.* **5**, 1996 (1966).
[17] G.B. Deacon and R.J. Philips, *Coord. Chem. Rev.* **33**, 227 (1980).