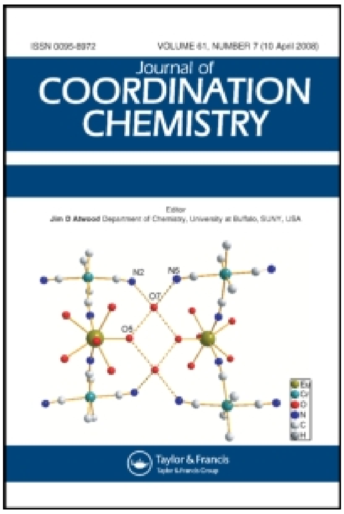

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Preparation, Structure and Thermal Decomposition of Cu(II) Complexes with 2-Chloro- and 2,3-Dichlorobenzoic Acids and Imidazole

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PREPARATION, STRUCTURE AND THERMAL DECOMPOSITION OF Cu(II) COMPLEXES WITH 2-CHLORO- AND 2,3-DICHLOROBENZOIC ACIDS AND IMIDAZOLE

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The reaction products of Cu(II) 2-chlorobenzoate and imidazole (**1**), and of Cu(II) 2,3-dichlorobenzoate and imidazole (**2**) formulated as $\mathrm{CuL'_2 \cdot 3imd}$ and $\mathrm{CuL''_2 \cdot 3imd}$ ($\mathrm{L' = C_7H_4ClO_2}$, $\mathrm{L'' = C_7H_4Cl_2O_2{}^-}$, imd = imidazole), were prepared and characterized by means of structural and spectroscopic measurements and thermochemical properties. The blue (**1**) and green (**2**) compounds crystallize in the monoclinic system with space group $C2/c$, cell parameters $a = 20.753(4)$, $b = 8.414(2)$, $c = 14.429(3)\,\text{Å}$, $\beta = 90.15(3)^\circ$, $V = 2519.5(9)\,\text{Å}^3$, $Z = 4$ for (**1**) and $a = 21.335(4)$, $b = 8.417(2)$, $c = 15.030(3)\,\text{Å}$, $\beta = 94.11(3)^\circ$, $V = 2692.1(10)\,\text{Å}^3$, $Z = 4$ for (**2**). The complexes decompose at 483 K.

Keywords: Copper; 2-Chlorobenzoic acid; 2,3-Dichlorobenzoic acid; Complexes; X-ray analysis; Thermal properties

INTRODUCTION

A general survey of the literature on complexes of Cu(II) with nitrogen donors reveals that a considerable amount of work has been carried out on the preparation and characterisation of addition complexes of Cu(II) carboxylates. During the course of this investigation some adducts of Cu(II) chlorobenzoate were prepared with 1,3-propanodiamine [1–3] and pyridine [4]. Carboxylates of divalent metals are noted to give, with various donor ligands, complexes of three different stoichiometries, *viz.*, 1 : 1, 1 : 2 and 1 : 4. In some cases a metal carboxylate may give adducts of two different stoichiometries with the same ligand under different experimental conditions [5,6]. Complexes of bridged *bis*(imidazole) and *bis*(benzimidazole) ligands of various bridge types with transition metals have been examined as potential models of the structure of metal binding sites in metalloproteins like haemerythrin, hemocyanin, tyrosinase or azurin [7–13]. One of these *N*-donor ligands is imidazole. This work is a continuation of our study on the structure and properties of metal complexes with dichlorobenzoic acids and *N*-donor ligands.

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EXPERIMENTAL

2-Chloro- and 2,3-dichlorobenzoates of Cu(II) were obtained by a modified method [14,15]. Basic Cu(II) carbonate ($CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, 0.01 mol) was added to a hot solution of 2-chlorobenzoic acid (0.02 mol in 0.2 dm^3 of water) and the suspension was heated with stirring for about 4 h. The same procedure was applied in the reaction of 2,3-dichlorobenzoate with Cu(II). After filtering the saturated solutions, the Cu(II) complexes were subjected to slow crystallization. The precipitates formed were filtered, washed with water and dried at 303 K to constant mass.

The title complexes were obtained by dissolving the Cu(II) complex with 2-chlorobenzoic acid (**1**) and of Cu(II) with 2,3-dichlorobenzoic acid (**2**) (0.01 mol) in 0.2 dm^3 of a 0.1 M solution of imidazole in water. The solutions were subjected to slow crystallization. Blue (**1**) and green (**2**) crystals suitable for X-ray data collection were deposited after three weeks. The products were filtered off, washed with water and dried at 303 K to constant mass. Carbon, hydrogen and nitrogen contents in the complexes were determined by elemental analysis using a Perkin Elmer CAN 2000 instrument. The chlorine content was measured by the Schöniger method. Cu(II) content was determined by AAS using an AAS-3 (Carl Zeiss-Jena). The experimental results are concordant with the calculated data [Cu 10.98 (10.9)%, C 47.71 (47.7)%, H 3.46 (3.3)%, Cl 12.27 (12.2)%, N 14.52 (14.6)%] for (**1**) and [Cu 9.82 (9.8)%, C 42.62 (42.6)%, H 2.78 (2.7)%, Cl 21.29 (21.2)%, N 12.97 (13.1)%] for (**2**).

Spectroscopic Measurements

IR spectra were recorded over the range 4000–400 cm^{-1} using a Perkin Elmer FT-IR 1725X spectrophotometer.

Thermochemical Properties

The thermal stabilities of the Cu(II) complexes were determined using a Paulik–Paulik–Erdey Q 1500 D derivatograph with a Derill converter; TG, DTG and DTA curves were recorded. Samples (100 mg) were heated in platinum crucibles to 1273 K in static air at a heating rate of 10 K min^{-1}.

X-ray Structure Determination

X-ray measurements for compounds (**1**) and (**2**) were made on a Kuma KM4 ℵ-axis four-circle diffractometer with a graphite monochromator using MoKα or CuKα radiation. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw) programs.

Crystallographic data and the refinement procedure details are given in Table I. The structures were solved by direct methods with SHELXS97 [16] and refined by full-matrix least-square methods on all F^2 data using the SHELXL97 [17] program. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the difference Fourier maps and refined with isotropic thermal parameters. The final refinement resulted in $R_1 = 0.0479$ for compound (**1**)

TABLE I Crystal data and structure refinement detail, for compounds (**1**) and (**2**)

	1	**2**
Empirical formula	$C_{23}H_{20}O_4Cl_2N_6Cu$	$C_{23}H_{20}O_4Cl_2N_6Cu$
Temperature (K)	293(2)	293(2)
Molecular weight	578.89	647.77
Wavelength (Å)	0.71073	1.54180
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	20.753(4)	21.335(4)
b (Å)	8.414(2)	8.417(2)
c (Å)	14.429(3)	15.030(3)
β (°)	90.15(3)	94.11(3)
V (Å^3)	2519.5(9)	2692.1(10)
Z	4	4
F (000)	1180	1308
D_m flotation (Mg/m^3)	1.52	1.60
D_c (Mg/m^3)	1.526	1.598
Crystal size (mm)	0.25 × 0.25 × 0.30	0.15 × 0.15 × 0.20
Diffractometer	Kuma KM4	Kuma KM4
2θ limit (°)	4–54	8–160
Ranges h	−26 to 26	−27 to 27
k	0 to 10	0 to 10
l	0 to 17	0 to 18
Reflections (unique)	1841	2696
Data [$I > 2\sigma(I)$]/parameters	1403/164	2214/210
GOF on F^2	1.084	1.062
R_1, wR_2 [$I > 2\sigma(I)$]	0.0479, 0.1402	0.0474, 0.1237
R_1, wR_2 indices (all data)	0.0641, 0.1449	0.0544, 0.1290
$\Delta^{-}\rho$/e Å^{-3}	0.360 and −0.590	1.078 and −0.597

and $R_1 = 0.0474$ for compound (**2**). Final fractional atomic coordinates for non-hydrogen atoms and equivalent isotropic thermal parameters are presented in Table II. Bond lengths and bond angles are listed in Table III.

RESULTS AND DISCUSSION

IR spectroscopic data for the compounds are summarized in Table IV. IR spectra of (**1**) and (**2**) shows three strong bands at 1328, 1072 and 952 cm^{-1}, due to valence C–N vibrations of imidazole. They are shifted toward higher energy compared with corresponding C–N vibrations of the uncoordinated ligand. The ν(Cu–N) band is observed at 652 cm^{-1} for (**1**) and 656 cm^{-1} for (**2**). These bands are observed neither in the IR spectra of free imidazole nor in Cu(II)-2-chlorobenzoate [14] or Cu(II)-2,3-dichlorobenzoate [15]. In the IR spectrum of the free acid there is a single strong absorption at 1688 cm^{-1} for (**1**) and for (**2**) (COOH group). In the IR spectrum of the title compounds, this absorption band disappears, and a split asymmetrical (COO^-) vibration (ν_{as}) at 1604 cm^{-1} as well as symmetrical vibrations (ν_s) at 1396 cm^{-1} for (**1**) and 1604 cm^{-1} and 1388 cm^{-1} for (**2**), respectively, appear. The split ν_{as} (COO^-) and ν_s (COO^-), as well as the separation ($\Delta\nu$) of ν_{as} (COO^-) and ν_s (COO^-) of 208 cm^{-1} for (**1**) and (222 cm^{-1} for (**2**) suggests that the carboxylate groups act as bidentate asymmetric ligand [18–20]. This was confirmed by X-ray analysis. The C–C and C–H vibrational bands of the Cu(II) complexes change their

TABLE II Atomic coordinates and equivalent isotropic displacement parameters for compounds (**1**) and (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	$U(eq)$
(**1**)				
Cu	0.5000	0.13882(6)	0.2500	0.0455(3)
Cl	0.34250(8)	0.32874(15)	– 0.03833(8)	0.0720(4)
O(1)	0.4349(1)	0.3177(3)	0.2074(2)	0.0471(7)
O(2)	0.3766(2)	0.1244(3)	0.1430(2)	0.0553(7)
N(1)	0.4576(1)	0.1455(3)	0.3738(2)	0.0385(6)
N(2)	0.4141(2)	0.0828(4)	0.5074(2)	0.0443(7)
N(3)	0.5000	– 0.1011	0.2500	0.0367(8)
NC$^{\#}$	0.5297(4)	– 0.3500(4)	0.2576(3)	0.086(2)
CN$^{\#}$	0.5297(4)	– 0.3500(4)	0.2576(3)	0.086(2)
C(1)	0.3335(2)	0.3858(4)	0.1461(3)	0.0430(8)
C(2)	0.3097(2)	0.4177(4)	0.0589(3)	0.0484(8)
C(3)	0.2591(2)	0.5252(6)	0.0476(5)	0.075(2)
C(4)	0.2339(3)	0.6022(6)	0.1203(6)	0.088(2)
C(5)	0.2561(3)	0.5710(7)	0.2102(5)	0.083(2)
C(6)	0.3860(2)	0.2657(4)	0.1659(2)	0.0396(7)
C(7)	0.3860(2)	0.2657(4)	0.1659(2)	0.0417(8)
C(8)	0.4395(2)	0.0290(4)	0.4289(2)	0.0396(7)
C(9)	0.4158(2)	0.2441(5)	0.5037(3)	0.0550(10)
C(10)	0.4427(2)	0.2817(4)	0.4221(3)	0.0538(9)
C(11)	0.5517(2)	– 0.1947(4)	0.2600(3)	0.0556(11)
(**2**)				
Cu	0.5000	0.13896(5)	0.2500	0.03235(19)
Cl(1)	0.36230(3)	0.32263(9)	0.52354(4)	0.0527(2)
Cl(2)	0.24388(3)	0.53085(11)	0.54713(5)	0.0610(3)
O(1)	0.4365(1)	0.3192(2)	0.2884(1)	0.0432(4)
O(2)	0.3881(1)	0.1152(2)	0.3481(1)	0.0475(5)
N(1)	0.4567(1)	0.1454(2)	0.1291(2)	0.0370(5)
N(2)	0.4167(1)	0.0783(3)	– 0.0037(2)	0.0459(5)
N(3)	0.5000	– 0.1022(3)	0.2500	0.0372(6)
CN	0.4703(2)	– 0.3488(3)	0.2585(3)	0.0739(12)
C(1)	0.3386(1)	0.3673(3)	0.3464(2)	0.0366(5)
C(2)	0.3197(1)	0.3967(3)	0.4303(2)	0.0330(5)
C(3)	0.2673(1)	0.4916(3)	0.4420(2)	0.0399(5)
C(4)	0.2331(1)	0.5526(4)	0.3693(2)	0.0548(7)
C(5)	0.2517(2)	0.5253(4)	0.2846(2)	0.0622(9)
C(6)	0.3050(1)	0.4348(4)	0.2733(2)	0.0541(7)
C(7)	0.3923(1)	0.2577(3)	0.3283(2)	0.0341(5)
C(8)	0.4434(1)	0.0270(3)	0.0729(2)	0.0408(5)
C(9)	0.4123(2)	0.2374(4)	0.0015(2)	0.0585(8)
C(10)	0.4367(2)	0.2787(3)	0.0827(2)	0.0574(8)
C(11)	0.4509(2)	– 0.1965(3)	0.2628(2)	0.0557(7)
C(10)	0.2427(2)	0.0624(3)	0.1220(2)	0.0363(4)

frequencies only insignificantly compared to the corresponding bands of imidazole and the free acids, thus indicating that the Cu(II) ion in the complexes does not deform the phenyl and imidazole rings to a noticeable extent, an assumption which was confirmed by the crystal structure determinations.

The structures of the compounds and numbering of atoms are shown in Figs. 1 and 2. The complex of copper(II) with imidazole and 2-chlorobenzoate ligands (**1**) is isostructural with that of copper(II) with imidazole and 2,3-dichlorobenzoate (**2**). They both crystallize in space group *C*2/*c*, with the Cu atom in a special position on the twofold rotation axis. Both structures show that one imidazole molecule is disordered and situated along a twofold axis with half-occupancy.

TABLE III Selected bond lengths (Å) and angles (°) for the complexes

	1	**2**
Cu–N(1)	1.994(3)	1.980(2)
Cu–N(1)i	1.994(3)	1.980(2)
Cu–N(3)	2.019(3)	2.030(2)
Cu–O(1)i	2.113(2)	2.141(2)
Cu–O(1)	2.113(2)	2.141(2)
O(1)–O(7)	1.255(5)	1.263(3)
O(2)–O(7)	1.249(4)	1.241(3)
N(1)–Cu–N(1)i	179.79(14)	176.84(10)
N(1)–Cu–N(3)	91.61(7)	91.58(5)
N(1)i–Cu–N(3)	91.61(7)	91.58(5)
N(1)–Cu–O(1)i	90.19(12)	89.77(8)
N(1)i–Cu–O(1)i	87.52(11)	87.99(8)
N(1)–Cu–O(1)	87.52(11)	87.99(8)
N(1)i–Cu–O(1)	90.19(12)	89.77(8)
O(1)i–Cu–O(1)	89.2(2)	89.77(10)
O(2)–C(7)–C(1)	118.3(3)	118.5(2)
O(1)–C(7)–C(1)	115.9(3)	115.9(2)
O(2)–C(7)–O(1)	125.7(3)	125.5(2)

Symmetry codes: i(**1**) $1-x$, y, $0.5-z$; i(**2**) $1-x$, y, $-z+0.5$.

TABLE IV Frequencies of characteristic absorption bands in the IR spectra of (**1**) and (**2**) and their precursors (cm^{-1})

2-CuL$'_2$·H$_2$O	*2,3-CuL$''$*	*imidazole*	**1**	**2**	*Assignment*
3444					ν(OH)
		3200–2624	3120–2892	3150–2944	ν(N–H)
		1668			ν(C=N)
1610					$\delta(H_2O)$
1596	1604		1604	1604	$\nu_{as}(OCO^-)$
1512	1512				ν(C···C)
1400	1400		1396	1388	ν_s (OCO^-)
		1326	1328	1328	ν(C–N)
1264	1280	1272	1264	1264	ν(C···C)
		1056	1072	1072	ν(C–N)
1040	1052	1048	1048	1048	ν(C···C)
		936,840	952,876	952,868	ν(C–N)
752	768		752	748	ν(C–Cl)
			652	656	ν(Cu–N)
728,512	520,472	660	456	496	ν(C–H)

The copper(II) ion forms a monomeric complex, coordinating three molecules of imidazole, each by the nitrogen atoms of the ring as well as two 2-chlorobenzoate ligands by their carboxylate groups. The distance Cu to N(3) is 2.030(2) Å and 1.980(2) Å to the remaining nitrogen atoms of imidazole ligands (N1, N1a). In the coordination polyhedron around the copper atom the angle N1–Cu–N1a is 174.84(10)° and N1–Cu–N3 is 91.58(5)°. The copper ion does not lie exactly in the imidazole ring plane, but 0.040(6) or 0.032(8) Å out of the plane.

The remaining atoms in the coordination sphere ion are oxygen atoms from the carboxylate groups of 2-chlorobenzoate ligands. Each carboxylate group coordinates with the copper atom in the same way. One (O1) bonds with the short distance

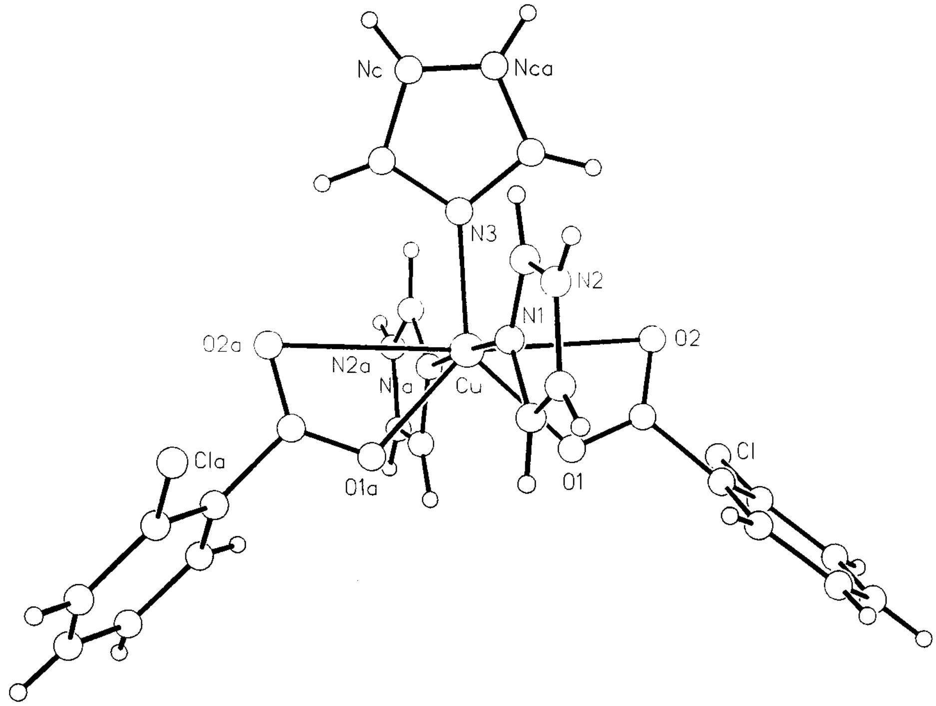

FIGURE 1 Molecular structure of $[Cu(C_7H_4ClO_2)_2 \cdot 3imd]$ (**1**).

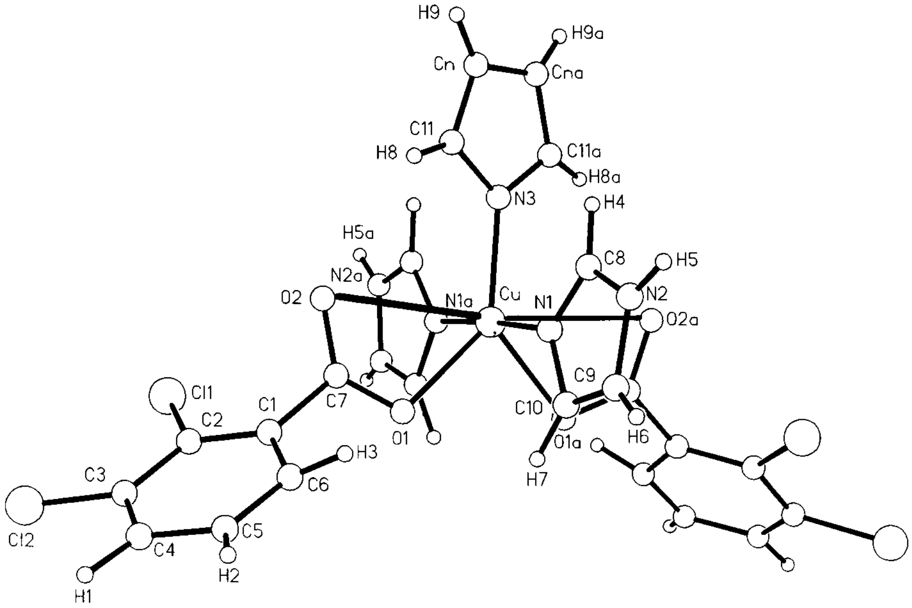

FIGURE 2 Molecular structure of $[Cu(C_7H_3Cl_2O_2)_2 \cdot 3imd]$ (**2**).

TABLE V Hydrogen bond parameter for compound (**1**) and (**2**) [(Å) and (°)]

D-H···A	*d (D-H)*	*d (H···A)*	*d (D···A)*	*< D-H···A*
(**1**)				
N(2)-H(6)···O(2) [x, $-y$, $0.5+z$	0.86	1.88	2.736(5)	171
N(C)-H(N)···O(1) [$1-x$, $-1+y$, $0.5-z$]	0.93	2.09	2.935(10)	151
(**2**)				
N(2)-H(5)···O(2) [x, $-y$, $z-0.5$	0.92	1.87	2.792(3)	174

2.141(2) Å. The second oxygen atom of each carboxylate group has a longer distance from copper 2.989(2) Å. The angle O1–Cu–O1a is 89.77(10)° but O2–Cu–O2a is near 180°. The formation of an angle of about 90° between the two short copper–oxygen bonds appears very rare in the structures of copper compounds [21].

The O–C–O angle in the carboxylate groups is 125.7(3)°, characteristic of bidentate-chelating carboxylate groups.

The phenyl rings form a planar system but due to metal coordination the carboxylic groups are rotated from the ring plane by 58.8(1)°. The copper cation does not lie in the carboxylate group plane, but 0.263(6) Å out of the plane. The distances and angles in the phenyl rings are the same as those for free chlorobenzoic acids.

The crystal structure of $CuL'_2 \cdot 3imd$ (**1**) consists of discrete units of the complex linked by two intermolecular hydrogen bonds of the type N–H···O (Table V), forming a stable network. The second complex of formula $CuL''_2 \cdot 3imd$ (**2**) possesses similar geometry and the bond distances and angles in both compounds differ only slightly, as shown in Table III.

Comparison of structural data reveals that the introduction of the second chloro-substituent at the ring in compound (**2**) has a negligible influence on these parameters.

The title complexes (**1**) and (**2**) are stable in air at room temperature and can be stored for several months in air. During heating they decompose in the same way. With a heating rate of $10\,\mathrm{K\,min^{-1}}$, the complexes are stable up to 483 K and then decompose to gaseous products (similar to Cu(II) complexes with 2,3- [15], 2,4- [22], 2,5- [23], 2,6- [24], 3,4- [21] and 3,5- [21] dichlorobenzoic acids).

Supplementary Material

Full lists of crystallographic data are available from the author on request.

References

[1] R. Uggla, O. Orama, N. Sundberg, E. Tirronen and N. Klinga (1974). *Finn. Chem. Lett.*, 185.

[2] N. Sundberg and R. Kivekas (1985) *Eur. Cryst. Meeting*, **9**, 309.

[3] H.L. Alten, G. van Koten, E. Riethorat and C.H. Stam (1989). *Inorg. Chem.*, **26**, 4141.

[4] K. Nakatani, J. Slecten, S. Halut-Desporte, S. Jeannin, Y. Jeannin and O. Kahn (1991). *Inorg. Chem.*, **30**, 164.

[5] N. Kitajima, K. Fujisawa and Y. Noro-oka (1990). *Inorg. Chem.*, **29**, 357.

[6] T. Kawatw, N. Yamanaka, S. Chba, T. Nichida, N. Nagamateu, T. Tokii and N. Kato (1992). *Bull. Chem. Soc. Jpn.*, **65**, 2739.

[7] H. Adams, A.B. Neil, J.D. Crane, D.E. Fenton, J.M. Latour and J.M. Wiliams (1990). *J. Chem. Soc. Dalton Trans.*, 1727.

[8] T.N. Sorrel and M.L. Garrity (1991). *Inorg. Chem.*, **30**, 210.

[9] S. Chen and J. Richardson (1994). *Inorg. Chem.*, **33**, 2376.
[10] S. Tandon, L. Thomson, J. Bridson and J. Dewan (1992). *Can J. Chem.*, **70**, 2771.
[11] J. Sessler, J. Hugdahl and B. Lynch (1991). *Inorg. Chem.*, **30**, 334.
[12] A. van Steenberger, E. Bouwman, A. de Graaf, W. Driessen, J., Reedijk and P. Zanello (1990). *J. Chem. Soc. Dalton Trans.*, 3175.
[13] J. Lockhart, W. Clegg, M. Hill and D. Rushton (1990). *J. Chem. Dalton Trans.*, 3541.
[14] T. Kawata, S. Chba, T. Tokii, Y. Mutto and M. Kato (1992). *Acta Cryst.*, **C48**, 1590.
[15] W. Wołodkiewicz and W. Brzyska (1998). *Polish J. Chem.*, **72**, 2366.
[16] G.M. Sheldrick (1997). SHELXS97 Program for Solution of Crystal Structures. University of Göttingen, Germany.
[17] Sheldrick, G.M. (1997). SHELXL97 Program for Crystal Structure Refinement University of Göttingen, Germany.
[18] A. Gross and R. Jones (1969). An introduction to Practical Infrared Spectroscopy. Butterworth, London.
[19] B. Manhas and A. Trikha (1982). *Indian J. Chem.*, **59**, 315.
[20] K. Nakamoto (1997). Infrared and Raman spectra of Inorganic Compounds. Wiley, New York.
[21] W. Wołodkiewicz, W. Brzyska and T. Głowiak (1998). *Monats. Chem.*, **129**, 111.
[22] W. Wołodkiewicz and W. Brzyska (1997). *Polish J. Chem.*, **71**, 16.
[23] W. Wołodkiewicz and W. Brzyska (1999). *J. Thermal Anal. Calorim.*, **55**, 639.
[24] W. Brzyska and W. Wołodkiewicz (1994). *Thermochim. Acta*, **242**, 131.
[25] W. Brzyska and W. Wołodkiewicz (1995). *Polish J. Chem.*, **69**, 1109.