Thermochimica Acta, 191 (1991) 95–104
Elsevier Science Publishers B.V., Amsterdam

The thermal behaviour of zinc and cadmium dihalide complexes with O- and S-donors

G. Faraglia [a], D. Fregona [a], Z.J. Guo [a,1] and S. Sitran [b]

[a] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università, via Loredan 4, 35100-Padova (Italy)*
[b] *Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, 35020-Padova (Italy)*

(Received 20 March 1991)

Abstract

The carbonyl donor 2,6-dimethyl-4H-pyran-4-one (DMP) reacts with zinc and cadmium dihalides to form the complexes $[Cd(DMP)Cl_2]_n$ and $[M(DMP)_2X_2]$ (M = Cd, X = Br or I; M = Zn, X = Cl, Br or I). On the basis of their infrared spectra, the 1:2 adducts should have a distorted tetrahedral configuration, whereas the $[Cd(DMP)Cl_2]_n$ complex probably has a polymeric structure formed by bridging chlorine atoms. The thermal behaviour of the DMP adducts is compared with that of the 2,6-dimethyl-4H-pyran-4-thione (DMTP) analogues of general formulae $[M(DMTP)_2X_2]$ (M = Cd or Zn; X = halide) and $[Cd(DMTP)Cl_2]_n$.

INTRODUCTION

As part of a study on metal complexes with carbonyl and thiocarbonyl donors, we have recently described the properties of zinc, cadmium and mercury dihalide adducts with 2,6-dimethyl-4H-pyran-4-thione (DMTP) of general formulae $[M(DMTP)_2X_2]$ and $[M(DMTP)X_2]_n$ (M = Zn, Cd or Hg; X = halide) [1,2]. The ligand acts as a strong sulphur donor in mercury complexes, whereas the M–S bond strength weakens in cadmium and zinc adducts. Moreover, mercury halides react with 2,6-dimethyl-4H-pyran-4-one (DMP) to form the polymeric complexes $[Hg(DMP)X_2]_n$ and $(HgX_2)_3(DMP)_2$, which easily release the weakly bound ligand molecules in solution [1]. Because zinc and cadmium interactions with O- and S-donors are of interest in biochemical systems, it was considered worthwhile to examine the thermal behaviour of both DMTP and DMP complexes. Literature reports of zinc and cadmium dihalide complexes with O-donors concern mainly urea

---

[1] On leave from the Department of Basic Courses, Agricultural University of Hebei, Baoding, People's Republic of China.

[3–6], amide [7–11], phosphine oxide [12] and pyridine *N*-oxide [13] derivatives, the related adducts having either 1:1 or 1:2 stoichiometry. The formation of intermediate species such as $(CdCl_2)_3(acetylurea)_2$ [4] has sometimes been observed. As a general trend, the ability to yield lower stoichiometry complexes seems to increase in the order Zn < Cd < Hg.

EXPERIMENTAL

DMP ($C_7H_8O_2$, 2,6-dimethyl-4*H*-pyran-4-one, Ega Chemie) was used as supplied. The $CdBr_2 \cdot 4H_2O$ was supplied by Fluka; the anhydrous zinc and cadmium dihalides were Janssen products. The DMTP (2,6-dimethyl-4*H*-pyran-4-thione) complexes were prepared by the methods reported in ref. 2.

Preparation of the complexes

The complex $[Cd(DMP)Cl_2]_n$ was prepared by the reaction of $CdCl_2$ and ligand (molar ratio 1:4) in acetone. After stirring (6 h), the suspension was filtered and the white solid was washed with small fractions of acetone. Attempts to obtain the 1:2 adduct by operating at higher molar ratios (up to 1:8) in methanol, dichloromethane, 1,2-dichloroethane or benzene failed, the reaction product being always the 1:1 species. By the reaction of $CdCl_2$ and ligand in dichloroethane at a molar ratio of 1:1, a mixture of $CdCl_2$ and the 1:1 complex was obtained.

The complex $[Cd(DMP)_2Br_2]$ was separated by adding DMP (2 mmol) to an acetone solution of $CdBr_2 \cdot 4H_2O$ (1 mmol in 5 cm^3). The white solid was filtered, washed with *n*-pentane and dried in vacuo (yield, 85%). It was also obtained by using a reagent molar ratio of 1:1 in acetone, whereas in dichloromethane or in dichloroethane, mixtures of cadmium bromide and 1:2 adduct were isolated.

The complex $[Cd(DMP)_2I_2]$ was prepared by adding DMP (4 mmol) to a CdI_2 solution in acetone (1 mmol in 4 cm^3). After stirring (3 h), the white solid was filtered, washed with a few drops of acetone and then with *n*-pentane (yield, 65%). Well formed crystals of the product separated with a low yield from a warm saturated solution of the reagents (molar ratio 1:1) in methanol. The compound was also obtained by stirring a CdI_2 suspension in a 1,2-dichloroethane solution of ligand (molar ratios from 1:2 to 1:6; yield, 85%). In the same solvent at 1:1 molar ratio, mixtures of 1:2 complex and unreacted salt were isolated.

The complexes $[Zn(DMP)_2X_2]$ (X = Cl or I) were prepared by slow evaporation of acetone solutions containing metal salt and ligand at molar ratios of 1:2. Under the same conditions, the reaction of $ZnBr_2$ and ligand took place in the heterogeneous phase with stirring (4 h). The white solid was filtered, washed with benzene and *n*-pentane and dried in vacuo.

Measurements

The IR spectra were recorded using Nicolet 5SXC FT–IR and Nicolet 20F far-IR spectrometers, in Nujol mulls between KBr and polyethylene discs. The NMR (^{1}H and ^{13}C) spectra were obtained with a JEOL FX 90Q spectrometer. The TG, DTG and DTA curves in air (flow rate 250 cm^3 min^{-1}, heating rate 5 °C min^{-1}) were recorded on a Netzsch STA 429 thermoanalytical instrument (reference material Al_2O_3). The melting points (uncorrected) were determined using a Büchi apparatus.

RESULTS AND DISCUSSION

The complexes (Table 1) were generally prepared in acetone by reaction of the appropriate metal halide with DMP at molar ratios varying from 1:2 to 1:4. They have a 1:2 stoichiometry, except for cadmium chloride which forms a 1:1 adduct also if a large excess of ligand is used. The thermal data for the complexes are presented in Table 2.

The thermograms of $[Cd(DMP)Cl_2]_n$ (Fig. 1) present two endotherms at 235 and 308 °C, due to step-wise evolution of the DMP molecule. The first weight loss corresponds to the release of 60% of the ligand, the residual amount being evolved completely at around 320 °C with formation of cadmium chloride. Salt sublimation starts at around 500 °C, the process being pronounced above the melting point (562 °C, c.f 568 °C from ref. 14). A $[Cd(DMP)Cl_2]_n$ sample was heated directly on the thermobalance crucible up to the end of the first endothermic process. The elemental analysis of the residual solid (C, 14.5%; H, 1.5%) was in accordance with the formation of $CdCl_2 \cdot 0.4DMP$ (C, 14.6%; H, 1.5%).

The complex $[Cd(DMP)_2Br_2]$ (Fig. 2) melts at 215 °C with the simultaneous release of one DMP molecule. The 1:1 adduct is probably formed as an intermediate, whose degradation follows a trend similar to that of the chloro derivative. In fact two close endotherms (at 240 and 263 °C) are observed in the DTA curve, due to the successive evolution of 0.6 and 0.4 DMP molecules, respectively. The residual cadmium bromide melts at 555 °C, sample vaporisation being complete at 650 °C.

A multi-step process has been reported for the thermal degradation of Cd(*N*,*N*,*N*′-trimethylethylenediamine)Cl_2, in which ligand evolution occurs in four stages in the 150–350 °C interval [15].

The thermograms of $[Cd(DMP)_2I_2]$ present a melting endotherm at 197 °C, the ligand being almost totally evolved in one step (308 °C), followed by sample sublimation. The melting of the cadmium iodide (387 °C from ref. 14) is hidden by the sublimation process, the DTA curve being meaningless.

The thermal behaviour of the cadmium halide–DMTP complexes present a quite different trend in which ligand degradation occurs. As an example,

TABLE 1

Analytical data and selected IR wavenumbers

Compound	m.p. [a] (°C)	Found (calculated)		Wavenumbers (cm^{-1})				
		C%	H%					
$[Cd(DMP)Cl_2]_n$ [b]	–	27.20(27.34)	2.78(2.62)	1673s	1594sh	1589s		1555vw
$[Cd(DMP)_2Br_2]$ [c]	219–221	32.41(32.31)	3.18(3.10)	1657s	1647sh	1587w	1565s	1556sh
$[Cd(DMP)_2I_2]$ [c]	197–201	27.42(27.36)	2.73(2.62)	1655s	1646sh	1585shm	1567s	1556sh
$[Zn(DMP)_2Cl_2]$ [d]	192–194	43.60(43.72)	4.48(4.19)	1649s		1570w		1529s
$[Zn(DMP)_2Br_2]$ [d]	196–198	35.36(35.51)	3.62(3.41)	1649s		1570w	1548sh	1534s
$[Zn(DMP)_2I_2]$ [d]	177–179	29.69(29.63)	2.99(2.84)	1649s		1570w	1550sh	1535s

[a] With decomposition. [b] $C_7H_8CdCl_2O_2$. [c] $C_{14}H_{16}CdX_2O_2$ (X = Br or I). [d] $C_{14}H_{16}X_2O_2Zn$ (X = Cl, Br or I).

TABLE 2

Thermal data for the complexes

Compound	Decomposition interval (°C)	TG weight loss (%)		DTA peak temperature (°C)
		Experimental	Calculated	
$[Cd(DMP)Cl_2]_n$	170–240	24.1	24.2 (0.6 DMP)	235 endo
	240–320	16.3	16.1 (0.4 DMP)	308 endo
	490–720	58.3		562 m
$[Cd(DMP)_2Br_2]$	160–225	38.2	23.8 (DMP)	215 m
	225–270		14.3 (0.6 DMP)	240 endo
		9.7	9.5 (0.4 DMP)	263 endo
	450–640	50.2		555 m
$[Cd(DMP)_2I_2]$	155–310	35.9	40.4 (2 DMP)	197 m, 308 endo
	310–570	61.5		[a]
$[Zn(DMP)_2Cl_2]$	150–600	97.5		197 m, 304 br, 438 exo, 515 exo, 594 exo
$[Zn(DMP)_2Br_2]$	170–580	98.2		197 m, (330, 400, 430) exo, 522 exo
$[Zn(DMP)_2I_2]$	160–550	98.7		177 m, (370, 401, 435) exo, 507 exo
$[Cd(DMTP)Cl_2]_n$	190–280	11.1	43.3 (DMTP)	229 endo
		7.5		(245, 270) endo
	280–453	26.8		310 sh, 377 exo
	500–730	38.4		512 endo, 700 endo br
	750–1200	17.1		Very broad endo
$[Cd(DMTP)_2Cl_2]$	160–252	11.9	30.2 (DMTP)	(197, 208) endo
		11.3		(229, 244) endo
	252–510	33.9		306 exo, 417 exo, 501 sh exo
	510–700	21.5		522 endo, 700 endo br
	750–1200	19.2		Very broad endo
$[Cd(DMTP)_2Br_2]$	180–265	16.2	25.4 (DMTP)	218 m
	265–640	58.6		[a]
	640–900	21.1		[a]
$[Cd(DMTP)_2I_2]$	180–300	18.3	21.7 (DMTP)	191 m
	300–560	81.7		512 exo
$[Zn(DMTP)_2Cl_2]$	180–260	22.2	33.6 (DMTP)	224 m
	260–540	65.2		435 sh, 499 exo
$[Zn(DMTP)_2Br_2]$	200–395	18.9	27.3 (DMTP)	226 m
	395–650	78.5		545 exo, 590 sh
$[Zn(DMTP)_2I_2]$	198–400	24.2	23.4 (DMTP)	212 m
	400–560	68.2		450 sh, 499 exo

[a] See text.

the TG curve of $[Cd(DMTP)Cl_2]_n$ shown in Fig. 3 shows two nearly equal steps, the corresponding endotherms being split in the last process. The corresponding weight loss (approx. 19%) is well below the expected amount for the release of the DMTP molecule (43.3%), whereas the subsequent

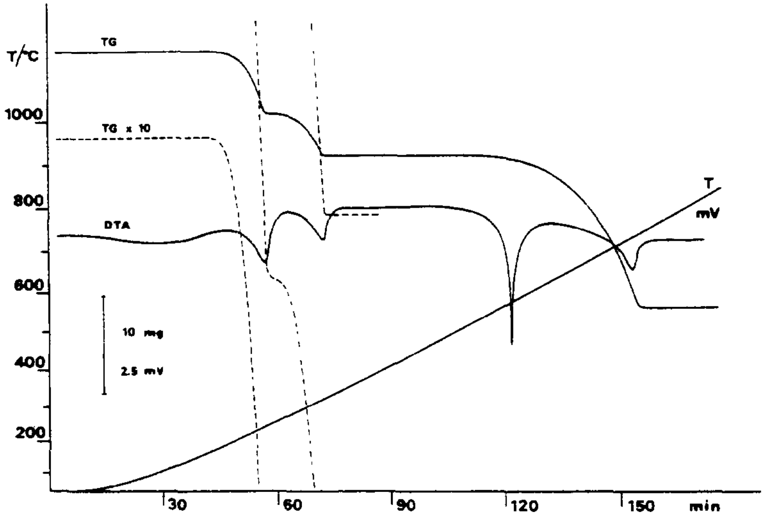

Fig. 1. Thermograms of $[Cd(DMP)Cl_2]_n$ in air (26.93 mg).

exothermic process (372 °C) is probably due to ligand combustion, as previously observed in the $[M(DMTP)_2X_2]$ (M = Pd or Pt; X = halide) thermograms [16]. The residue at around 550 °C is probably a mixture of cadmium halide and sulphide, the degradation process ending at around 1200 °C. The degradation of $[Cd(DMTP)_2Cl_2]$ follows a similar trend, except for ligand combustion, which occurs in the 300–500 °C interval. At higher temperatures, the thermograms of both compounds practically superimpose, suggesting the formation of a common intermediate mixture. Conversely, the $[Cd(DMTP)_2X_2]$ (X = Br or I) complexes melt with partial

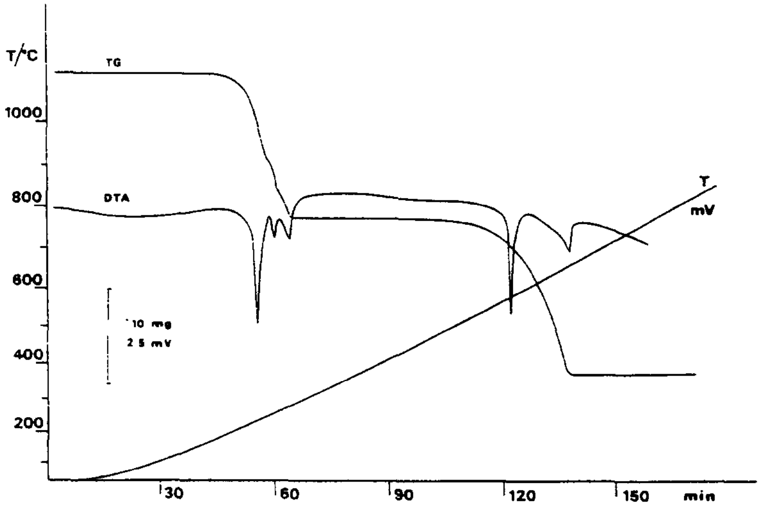

Fig. 2. Thermograms of $Cd(DMP)_2Br_2$ in air (30.90 mg).

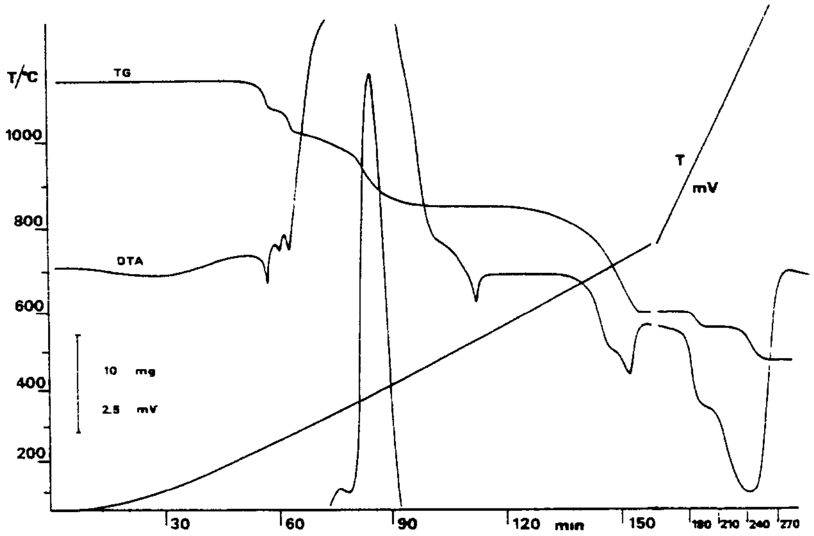

Fig. 3. Thermograms of $[Cd(DMTP)Cl_2]_n$ in air (28.73 mg).

ligand release. At higher temperatures, the combined effect of ligand combustion and sample sublimation causes a general flatness in the DTA curves. A similar behaviour is observed for the $[Zn(DMTP)_2X_2]$ (X = Cl, Br or I) complexes, whose degradation ends below 650 °C, leaving, in most cases, a non-stoichiometric residue, whereas $[Zn(DMP)_2X_2]$ samples vaporise in the 150–600 °C temperature interval.

The infrared spectrum of DMP contains two strong absorptions at 1669 and 1611 cm^{-1}, which have been assigned as ν(C=C) and ν(C=O) respectively, whereas the shoulder at 1599 cm^{-1} is due to ring vibrations [17]. These bands undergo a low energy shift on coordination, of the order of 10–20 cm^{-1} for ring absorptions. The position of the ν(C=O) bands is related to the metal–oxygen bond strength, being observed at low energy (1530 cm^{-1}) in the strongly bound $UO_2(DMP)_2(NO_3)_2$ complex and at around 1550 cm^{-1} for the lanthanide, $Ln(DMP)_3(NO_3)_3$, adducts [18]. Such a band falls at around 1534 cm^{-1} in the $[Zn(DMP)_2X_2]$ complexes (Table 1) and at around 1566 cm^{-1} in the cadmium analogues, whereas it is observed at high energy (1589 cm^{-1}) in $[Cd(DMP)Cl_2]_n$ with respect to the mercury 1:1 adducts (1568 cm^{-1}). The trend confirms an increasing ability to bind oxygen in the order Hg < Cd < Zn, as for ureas and amides. In the far infrared region (Table 3), the zinc complexes show two bands assignable to metal–halide bond vibrations. These bands, observed at high energy (Cl, 322 and 297 cm^{-1}; Br, 246 and 224 cm^{-1}) with respect to the corresponding absorptions in $[Zn(DMTP)_2X_2]$ (X = Cl, 300 and 276 cm^{-1}; X = Br, 229 and 201 cm^{-1}) should orginate from the Zn–X symmetric and asymmetric vibration modes in a distorted tetrahedral arrangement, confirmed for $[Zn(DMTP)_2Cl_2]$ by X-ray crystallography [2]. Moreover the related wave-

TABLE 3

IR wavenumbers in the 400–100 cm^{-1} region (ν(M–hal) in italics)

Compound	Wavenumbers (cm^{-1}) [a]												
$[Cd(DMP)Cl_2]_n$	364w			286w		213wbr		*189m*		*166sbr*		141vw	113mw
$[Cd(DMP)_2Br_2]$	359m			281mw	229wsh	*214ms*	202sh	196vvw	*183mw*	164w	150w	141w	115mw
$[Cd(DMP)_2I_2]$	356m			277mw	224mw	209w	200sh	195sh	*176m*	162w	*146mw*	124w	107mw
$[Zn(DMP)_2Cl_2]$	386m	*322ms*	*297m*	284mw	219s			193w				125ms	
$[Zn(DMP)_2Br_2]$	371m			279mw	*246ms*	*224ms*	200sh	192w					110w
$[Zn(DMP)_2I_2]$	369m			279mw		*206sbr*	200sh	193sh			148vvw		105vw

[a] w, weak; m, medium; s, strong; v, very.

TABLE 4

NMR data for the zinc complexes ($CDCl_3$, ppm, $T = 25\,°C$)

Compound	^1H-NMR		^{13}C-NMR			
	CH	CH_3	CO	COC	CH	CH_3
DMP	6.01	2.21	179.0	164.7	112.7	18.8
$[Zn(DMP)_2Cl_2]$	6.73	2.39	183.2	169.6	113.7	20.2
$[Zn(DMP)_2Br_2]$	6.76	2.39	183.3	169.4	113.7	20.2
$[Zn(DMP)_2I_2]$	6.80	2.40	183.1	169.6	113.7	20.3
$[Zn(DMP)_2I_2]$ [a]	6.65	1.33	183.3	169.0	113.8	19.0

[a] In deuterated benzene.

numbers agree well with those of pseudo-tetrahedral zinc complexes with monodentate and bidentate nitrogen donors [15,19,20]. As regards 1:2 cadmium halide adducts, they can display either a distorted tetrahedral configuration, favoured for X = I, or an octahedral arrangement through halide bridges, quite common for X = Cl, see ref. 2 and refs. cited therein. On the basis of literature data comparison, the $[Cd(DMP)_2X_2]$ complexes (X = Br, 214 and 183 cm^{-1}; X = I, 176 and 146 cm^{-1}) should have a tetrahedral configuration, as for the DMTP analogues (X = Br, 194 and 177 cm^{-1}; X = I, 169 and 134 cm^{-1}). In the presence of a polymeric octahedral arrangement, the related terminal and bridging metal–halide absorptions should appear at noticeably lower energies. Such a configuration should be present instead in $[Cd(DMP)Cl_2]_n$, whose Cd–Cl absorptions (189 and 166 cm^{-1}) are close to those of the $[Cd(DMTP)Cl_2]_n$ anologue (191 and 166 cm^{-1}).

The proton-NMR spectrum of DMP (Table 4) contains the singlets due to the methyl (2.21 ppm) and ring CH (6.01 ppm) protons. On coordination, both signals shift downfield, the effect being more evident for the CH resonance. The $[Zn(DMP)_2X_2]$ spectra are in accordance with a coordinated ligand in $CDCl_3$ and, in the case of $[Zn(DMP)_2I_2]$, in deuterated benzene, whereas the complexes tend to decompose in coordinating solvents such as methanol or acetone. The cadmium complex spectra have not been measured owing to their low solubility in chlorinated hydrocarbons. The trend in the ^{13}C-NMR spectra resembles that observed in the proton-NMR spectrum series. In fact the carbonyl C=O resonance undergoes a downfield shift with respect to free DMP (approx. 183 ppm against 179.0 ppm), as for the signal of the carbon atoms bound to the ring oxygen (approx. 169 ppm against 164.7 ppm), whereas the methyl and ring CH resonances are nearly unchanged.

ACKNOWLEDGEMENT

One of the authors (Z.J.G.) thanks the Ministero degli Affari Esteri of Italy for an annual grant.

REFERENCES

1 G. Faraglia, Z. Guo and S. Sitran, Polyhedron, 10 (1991) 351.
2 G. Faraglia, R. Graziani, Z. Guo, U. Casellato and S. Sitran, Inorg. Chim. Acta, in press.
3 C. Airoldi, A.P. Chagas and F.P. Assuncao, Can. J. Chem., 60 (1982) 2132.
4 Yu.Ya. Kharitonov and T.N. Gushchina, Russ. J. Inorg. Chem., 32 (1987) 226.
5 M.R.M.C. Santos and C. Airoldi, Thermochim. Acta, 125 (1988) 295.
6 Z.S. Muksumova, N.O. Orozbaeva, Ya.D. Fridman, A.K. Molodkin and K. Rysmendeev, Russ. J. Inorg. Chem., 31 (1986) 1647.
7 O.A. De Oliveira, A.P. Chagas and C. Airoldi, Inorg. Chem., 22 (1983) 136.
8 D.B. Powell and A. Woollins, Spectrochim. Acta Part A, 41 (1985) 1023.
9 T.P. Kim, B.I. Imanakunov and S.A. Kazybaev, Russ. J. Inorg. Chem., 30 (1985) 1604.
10 A.N. Smirnov, A.Yu. Tsivadze, G.V. Tsintsadze, Ts.G. Khugashvili and R.N. Shchelokov, Russ. J. Inorg. Chem., 25 (1980) 1770.
11 A. Berdiev, B.I. Imanakunov, S.A. Kazybaev and B. Abdybakirova, Russ. J. Inorg. Chem., 30 (1985) 1309.
12 Y. Hase and O.L. Alves, J. Mol. Struct., 50 (1978) 293.
13 M.L.C.P. Da Silva, A.P. Chagas and C. Airoldi, J. Chem. Soc., Dalton Trans., (1988) 2113.
14 R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Boca Raton, Florida (1983-1984).
15 N.A. Bell, Inorg. Chim. Acta, 141 (1988) 173.
16 G. Faraglia, F. Barbaro and S. Sitran, Transition Met. Chem., 15 (1990) 242.
17 A.R. Katritzky and R.A. Jones, Spectrochim. Acta, 17 (1961) 64.
18 S. Sitran, D. Fregona and G. Faraglia, J. Coord. Chem., 20 (1989) 193.
19 W.L. Steffen and G.J. Palenik, Inorg. Chem., 16 (1977) 1119.
20 F. Cariati, G. Ciani, L. Menabue, G.C. Pellacani, G. Rassu and A. Sironi, Inorg. Chem., 22 (1983) 1897.