Thermal Stability and Spectral Properties of Pyrazine-2,3-dicarboxylatocopper(II) Complexes with Ronicol

[a]S. C. MOJUMDAR, [b]K. LEBRUŠKOVÁ, and [b]D. VALIGURA

[a]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-845 36 Bratislava*
e-mail: scmojumdar@hotmail.com

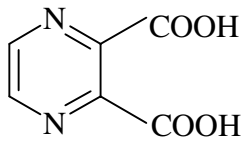
[b]*Department of Inorganic Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-812 37 Bratislava*

Received 5 February 2002

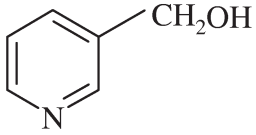
This paper reports an investigation of thermal and spectral properties of the complexes Cu(2,3-pdc) $\cdot$ $^1/_2H_2O$ (*I*), Cu(2,3-Hpdc)$_2 \cdot 2H_2O$ (*II*), and Cu(2,3-Hpdc)$_2$(ron)$_2$ (*III*) (where 2,3-Hpdc = monoanion and 2,3-pdc = dianion of pyrazine-2,3-dicarboxylic acid and ron = ronicol (3-pyridylmethanol)). TG, DTG, DTA, IR, and electronic spectra have been applied to investigate thermal and spectral properties of these complexes. The chemical composition of the complexes, the solid intermediates, and the resultant products of thermolysis have been identified by means of elemental analysis and complexometric titration. Schemes of destruction of these complexes are suggested. Heating of these compounds first resulted in a release of water molecules. The thermal stability of these complexes increases in the sequence: *I*, *II*, *III*. The final product of the thermal decomposition was CuO in all cases. IR data suggested a unidentate coordination of carboxylates to Cu(II) in complexes *I*—*III*.

The ability of different pyrazinecarboxylic acids (2-pyrazinecarboxylic acid, pyrazine-2,3-dicarboxylic acid, *etc.*) to act as chelating and bridging ligands for different metal ions is well known and has been extensively studied during last few decades [1—8]. The α-carboxylato groups increase pyrazine ligand coordination ability and influence of carboxylato group(s) addition to pyrazine ring on spectral and magnetic properties, thermal decomposition and of course on the structure of transition metal (chromium(III), and all metal(II) from manganese to zinc) complexes [1—8]. Little data are available on copper(II) complexes containing anions of pyrazine-2,3-dicarboxylic acid and ronicol. Such complexes are very interesting from both the chemical and biological points of view.

To reveal the relationship between the structure and thermolysis of metal carboxylate complexes, the study of the influence of metal and ligand nature upon the process of thermal decomposition is of a certain interest [9—14]. The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions and origin and preparation history [15, 16]. It is not surprising, therefore, that many authors have investigated metal and pyrazinedicarboxylate ligand bonds nature by examination of their thermal properties [1, 5, 6, 8]. In our previous papers we described the thermoanalytical properties of Mg(II), Cu(II), and Fe(III) complexes with pyridine and its derivatives [17—27]. It is interesting and well known [1] that pyrazinedicarboxylates form different hydrates and their stoichiometry and structure also have influence upon their reactivity. That was the reason why we included reactions from starting materials into our study under the same experimental conditions. Therefore, this paper describes the preparation of complexes formed by the ronicol and pyrazinedicarboxylate anions with Cu(II), along with thermal analyses and spectral investigation of prepared complexes.



Pyrazine-2,3-dicarboxylic acid (2,3-H_2pdc)



Ronicol (ron)

EXPERIMENTAL

Commercially available samples of pyrazine-2,3-dicarboxylic acid and ronicol (Aldrich) and copper(II) acetate (Lachema) were used as received.

The contents of carbon and hydrogen were determined by elemental analysis and the contents of copper were determined by complexometric titration.

Thermal decompositions of the complexes were conducted using a T.A.I. SDT 2960 instrument. Measurements were carried out between room temperature

Table 1. Chemical Analyses Data of the Compounds

Complex	w_i(calc.)/(%) w_i(found)/(%)			
	C	H	N	Cu
Cu(2,3-pdc) · $^1/_2H_2O$ (*I*)	30.20	1.27	11.74	26.63
	30.58	1.17	11.93	26.56
$Cu(2,3\text{-Hpdc})_2 \cdot 2H_2O$ (*II*)	33.23	2.32	12.92	14.65
	33.21	2.06	12.75	14.32
$Cu(2,3\text{-Hpdc})_2(ron)_2$ (*III*)	46.80	3.27	13.64	10.32
	46.69	3.24	13.58	10.25

and 1000 °C in a dynamic atmosphere of air, using a heating rate of 10 °C min^{-1}, sample mass 10—20 mg.

Electronic spectra in the λ-region 200—11000 nm were measured with a Specord 200 spectrophotometer. IR spectra in the $\tilde{\nu}$-region 200—4000 cm^{-1} were recorded by means of a Nicolet Magna 750 FTIR spectrometer. In both measurements the Nujol suspension technique was used, and IR spectra were recorded also by KBr technique and no significant difference was found.

Complexes *Cu(2,3-pdc)* · $^1/_2H_2O$ (*I*) and *Cu(2,3-Hpdc)*$_2$ · *2H*$_2$*O* (*II*) were prepared by addition of a stoichiometric amount of pyrazine-2,3-dicarboxylic acid (1.68 g 2,3-H_2pdc, 10 mmol in the case of *I* or 3.36 g 2,3-H_2pdc, 20 mmol in the case of *II*) to the solution of copper acetate (2.00 g $Cu(CH_3COO)_2 \cdot H_2O$, 10 mmol) in water (100 cm^3). The reaction mixture was stirred with the magnetic stirrer and the precipitation of light green *I*, or light blue *II* coloured products occurred. After a few hours the stable coloured products were filtered off, washed with water and dried in air.

Cu(2,3-Hpdc)$_2$*(ron)*$_2$ (*III*) was prepared by reaction of *II* (0.43 g; 1 mmol) and ronicol (3 cm^3). The reaction mixture was heated under condenser and stirred with the magnetic stirrer and the light blue coloured product was obtained. The product was filtered off, washed with acetonitrile to remove adsorbed ronicol and dried in air.

RESULTS AND DISCUSSION

The pyrazine-2,3-dicarboxylic acid (abbreviated as 2,3-H_2pdc throughout this paper) can form mono- or dianions and both copper(II) salts, pyrazinedicarboxylatocopper(II) and bis(hydrogenpyrazinedicarboxylato)copper(II), have been prepared depending on the synthesis condition. In spite of different coordination mode of the pyrazinedicarboxylato groups both copper(II) complexes exhibit polymeric, but distinct crystal structures [1]. Complexes of 1 : 1 stoichiometry $[M(2,3\text{-pdc})(H_2O)_2]_n \cdot 2nH_2O$ (M = Co, Ni, and Cu) contain infinite chains of metal atoms bridged with pdc anions and two carboxyl groups and two pyrazine nitrogen atoms are involved in bond formation and two water molecules complete pseudooctahedral coordination polyhedra. However, the complex of 1 : 2 stoichiometry $[Cu(2,3\text{-Hpdc})_2]_n \cdot 2nH_2O$ contains copper(II) atoms *trans*-coordinated by two chelating Hpdc anionic ligands thus forming square planar $Cu(2,3\text{-Hpdc})_2$ units which are in both axial positions coordinated by the nonprotonated oxygen atoms of protonated carboxylate group of neighbouring $Cu(2,3\text{-Hpdc})_2$ units. This results in infinite chain of copper(II) atoms linked by double-bridging Hpdc anions.

The mentioned polymeric structures of both copper(II) pyrazinedicarboxylates allow us to understand very high stability and very low solubility of both starting materials resulting in their very low reactivity in complex formation with some other neutral ligands. Only reactions of liquid ronicol with solid copper(II) salts give satisfactory product formation and this paper describes the preparation of copper(II) complex formed by the ronicol and pyrazinedicarboxylate anions.

The results of elemental analysis of the compounds given in Table 1 are in good agreement with theoretical expectations. Analytical data of complexes *I* and *II* showed us that in spite of similar preparation methods our products differ from published ones [1] in water content and that was proved also by their thermal decomposition (see below).

The thermal decomposition data of the complexes *I*—*III* are collected in Table 2. The complexes *I*—*III* are thermally relatively stable. Thermal decompositions of the compounds are multistage processes. The subsequent detachment of the ligands was observed. The final solid product was always identified as CuO.

The TG and DTA curves for the decomposition of *I* are shown in Fig. 1. The TG curve indicates that it is thermally stable up to 40 °C. Afterwards, the TG curve shows two mass fraction loss steps. The first step between 40 °C and 235 °C is accompanied by 3.53 % mass fraction loss, which is attributed to the dehydration process. The second step took place between 235 °C and 380 °C and is accompanied by 64.34 % mass fraction loss. It is attributed, however, to the oxidative decomposition of the anhydrous complex to CuO as

Table 2. Thermal Decomposition Data

Complex	DTA results			TG results		
	θ_{peaks}/℃		θ_{range}/℃	Mass fraction loss/% Found (calc.)	Loss of	Residue Found (calc.)/%
$Cu(2,3\text{-pdc}) \cdot {}^1/_2H_2O$	51	endo	40—235	3.53 (3.63)	$^1/_2H_2O$	CuO
	327	exo	235—380	64.34 (63.04)	decomposition of 2,3-pdc	32.10 (33.33)
$Cu(2,3\text{-Hpdc})_2 \cdot 2H_2O$	102	endo	42—158	8.53 (8.31)	$2H_2O$	CuO
	348	exo	158—391	71.96 (72.31)	decomposition of 2,3-Hpdc	19.45 (18.34)
$Cu(2,3\text{-Hpdc})_2(ron)_2$	230	endo	133—258	62.06 (62.72)	2ron + 2,3-H_2pdc	CuO
	327	exo	258—362	27.44 (24.37)	decomposition of 2,3-pdc	10.50 (12.91)

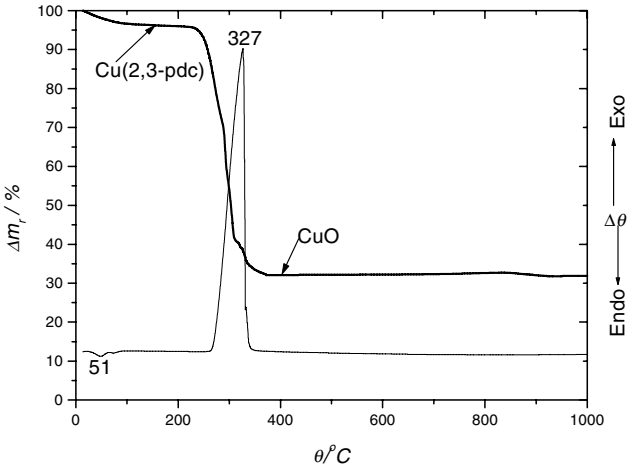


Fig. 1. TG — and DTA — curves of $Cu(2,3\text{-pdc}) \cdot {}^1/_2H_2O$ (*I*).

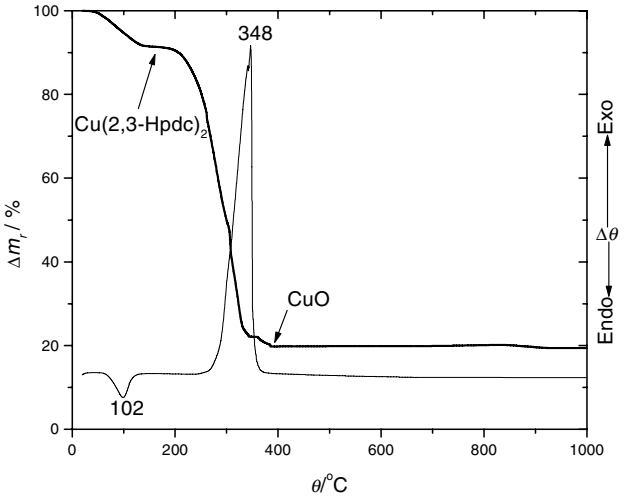


Fig. 2. TG — and DTA — curves of $Cu(2,3\text{-Hpdc})_2 \cdot 2H_2O$ (*II*).

the final solid product. The thermal reaction of complex *I* can be represented as

$$Cu(2,3\text{-pdc}) \cdot {}^1/_2H_2O \xrightarrow{40-235\,℃} Cu(2,3\text{-pdc})$$
$$Cu(2,3\text{-pdc}) \xrightarrow{235-380\,℃} CuO$$

The DTA curve for complex *I* shows an endothermic peak at 51℃ ascribed to the loss of H_2O, and an intensive exothermic peak maximized at 327℃ ascribed to the oxidative decomposition of Cu(2,3-pdc) with the formation of CuO.

The TG and DTA curves for the decomposition of *II* are shown in Fig. 2. The TG curve indicates that it is thermally stable up to 42℃. Afterwards, the TG curve shows two mass fraction loss steps. The first step between 42℃ and 158℃ is accompanied by 8.53 % mass fraction loss, which is attributed to the dehydration process. The second step between 158℃ and 391℃ is complicated and is accompanied by 71.96 % mass fraction loss. It is attributed, however, to the decomposition of the anhydrous complex $Cu(2,3\text{-Hpdc})_2$ to CuO as the final solid product. The thermal reaction of complex *II* can be represented as

$$Cu(2,3\text{-Hpdc})_2 \cdot 2H_2O \xrightarrow{42-158\,℃} Cu(2,3\text{-Hpdc})_2$$
$$Cu(2,3\text{-Hpdc})_2 \xrightarrow{158-391\,℃} CuO$$

The DTA curve for complex *II* shows an endothermic peak at 102℃ ascribed to the loss of $2H_2O$, and an exothermic peak maximized at 348℃ ascribed to the oxidative decomposition reaction of $Cu(2,3\text{-Hpdc})_2$ with the formation of CuO.

The TG and DTA curves for the decomposition of *III* are shown in Fig. 3. The TG curve indicates that it is thermally stable up to 133℃. Afterwards, the TG curve shows two mass fraction loss steps. The first step between 133℃ and 258℃ is accompanied by 62.06 % mass fraction loss. It is attributed to the loss of both ronicol molecules together with one 2,3-H_2pdc molecule. The second rather complicated step took place between 258℃ and 362℃ and is accompanied by 27.44 % mass fraction loss. This step is attributed, however, to the oxidative decomposition of

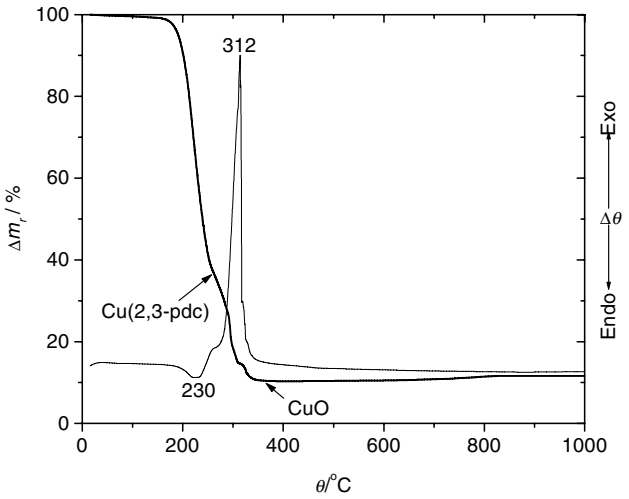


Fig. 3. TG — and DTA — curves of $Cu(2,3\text{-Hpdc})_2(ron)_2$ (*III*).

the anhydrous complex Cu(2,3-pdc) to CuO as the final solid product. The thermal decomposition of complex *III* can be represented as

$$Cu(2,3\text{-Hpdc})_2(ron)_2 \xrightarrow{133-258\,^{\circ}C} Cu(2,3\text{-pdc})$$

$$Cu(2,3\text{-pdc}) \xrightarrow{258-362\,^{\circ}C} CuO$$

The DTA curve for complex *III* shows an endothermic peak at 230 °C ascribed to the loss of 2 ronicol molecules together with 2,3-H_2pdc molecule, followed by an exothermic peak maximized at 327 °C. This exothermic peak is ascribed to the decomposition reaction of Cu(2,3-pdc) with the formation of CuO.

The UV absorptions of *I*—*III* could be assigned to π—π^* transitions of the aromatic system of pyrazinedicarboxylate anions bonded to copper(II) atom. All compounds exhibit shoulders between 370—420 nm that could be assigned as charge—transfer and thus attributed to the characteristic bridging system with the antiferromagnetic interaction [28].

Visible spectrum of the light green *I* and light blue compounds *II* and *III* exhibits and weak and very broad and asymmetrical *d*—*d* transition bands with maxima at 611 nm and 621 nm, respectively (Table 3). All compounds exhibit weak and unresolved shoulders at lower-energy side that are consistent with the proposed pseudooctahedral structure [1, 29]. It is interesting that ronicol complex formation in the presence of monoanion of pyrazine-2,3-dicarboxylic acid results in decreasing of *d*—*d* transition wavelength.

Table 3. Selected Electronic Spectral Data

Compound	Electronic spectra[a] λ/nm
$Cu(2,3\text{-pdc}) \cdot {}^1\!/_2H_2O$ (*I*)	410 sh, 611
$Cu(2,3\text{-Hpdc})_2 \cdot 2H_2O$ (*II*)	372 sh, 635
$Cu(2,3\text{-Hpdc})_2(ron)_2$ (*III*)	401 sh, 621

a) sh = shoulder.

The most important infrared spectral data of compounds *I*—*III* are reported in Table 4. The IR spectra of compounds *I*—*III* showed broad absorption bands in the range 3100—3600 cm^{-1}. These frequencies correspond to the antisymmetric and symmetric OH stretching vibrations [30, 31]. These bands clearly confirm the presence of water or ronicol in these compounds. Lower temperature of water evolution from *I* is in good agreement with infrared spectral data that suggested the presence of lattice water (HOH bending vibration at 1676 cm^{-1}) in comparison to compound *II* where coordinated water molecules are suggested.

The stretching vibration of the C═N in the pyridine ring was found at 1597 cm^{-1} and upon the complex formation the peak shifts to higher frequencies [32]. The shifts to about 1607 cm^{-1} may suggest bond formation by metal with the nitrogen of heterocyclic ring [33].

Carboxylate ions can coordinate to metal ions in a number of ways such as unidentate, bidentate (chelating) or bridging. The analysis of COO^- group bands allowed the determination of the parameter $\Delta_{COO} = \tilde{\nu}(COO^-_{as}) - \tilde{\nu}(COO^-_{s})$. The magnitude of Δ_{COO} has been used by *Nakamoto* [34] as a criterion to decide which way carboxylates bind to metal ions. From the IR spectra calculated values of Δ_{COO} were

Table 4. Infrared Spectral Data (200—4000 cm^{-1}) of Complexes *I*—*III*

Assignment	Ronicol	*I*	*II*	*III*
$\tilde{\nu}(COO^-_{as})/cm^{-1}$	–	1647	1702, 1652	1666, 1606
$\tilde{\nu}(COO^-_{s})/cm^{-1}$	–	1327	1354, 1324	1385, 1328
Δ_{COO}	–	320	348, 328	281 278
$\tilde{\nu}(CN)/cm^{-1}$	1597	–	–	1607
$\tilde{\nu}(OH)/cm^{-1}$	3226, 3371 sh	3210 br	3211	3203, 3391 sh

as = antisymmetric, s = symmetric.

close to 300 cm^{-1}. These values are in good agreement with the literature data for monodentate mode of covalently bonded carboxylato group of pyrazine-2,3-dicarboxylato anions [34, 35]. On the other hand, our values of $\tilde{\nu}(COO^-)$ vibrations are similar to those found in literature [6] but the thermal decomposition of anions proceeds without the mass loss step attributed to CO_2 evolution as a consequence of protonated carboxyl group thermal instability.

The complexes *I*, *II* are hydrated and complex *III* does not contain any water molecules. All complexes *I*—*III* showed reasonable stability in air. They exhibit a very low solubility in water and in ethanol, methanol, acetonitrile, and dimethylsulfoxide. The decompositions of compounds *I* and *II* were initiated by elimination of water. Then for complexes *I* and *II* decomposition of pyrazine-2,3-dicarboxylate anions occurs (on the TG curves) in one or more steps. The decomposition of compound *III* continued by elimination of ronicol molecules simultaneously with decomposition of pyrazine-2,3-dicarboxylato anions. The thermal stability of the complexes can be ordered in the sequence: *I*, *II*, and *III*. The results revealed that CuO was left as residue at the end of the thermal degradation experiments with complexes *I*—*III*. The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions, origin, and preparation history [15, 16]. By means of spectral analyses the structures of the compounds have been studied. Infrared data suggested that one oxygen atom of carboxylate ions is used for coordination to Cu(II) and the other one is probably not used in bond formation. Without X-ray analysis, no definite structure can be described for the different components. However, spectroscopic and analytical data together with the thermal analyses techniques enabled us to predict structures of these complexes.

Acknowledgements. We wish to thank the Ministry of Education of the Slovak Republic for financial support.

REFERENCES

1. Mao, L., Rettig, S. J., Thompson, R. C., Trotter, J., and Xia, S., *Can. J. Chem. 74*, 433 (1996).
2. Chapman, R. Z., Stephens, F. S., and Vagg, R. S., *Inorg. Chim. Acta 26*, 247 (1977).
3. O'Connor, C. J. and Sinn, E., *Inorg. Chem. 20*, 545 (1981).
4. Kuramoto, H. and Inoue, M., *Inorg. Chim. Acta 32*, 209 (1979).
5. Matthews, R. W. and Walton, R. A., *Inorg. Chem. 10*, 1433 (1971).
6. Magri, A. L., Magri, A. D., Balestrieri, F., Cardarelli, E., D'Ascenzo, G., and Panzanelli, A., *Thermochim. Acta 48*, 253 (1981).
7. Richard, P. P., Tran Qui, D., and Bertraut, E. F., *Acta Crystallogr., Sect. B 29*, 1111 (1973).
8. Magri, A. L. and Magri, A. D., *Thermochim. Acta 38*, 225 (1980).
9. Jóna, E., Kubranová, M., Šimon, P., and Mroziński, J., *J. Therm. Anal. 46*, 1325 (1996).
10. Jóna, E., Sirota, A., Šimon, P., and Kubranová, M., *Thermochim. Acta 258*, 161 (1995).
11. Hanic, F., Horváth, I., and Plesch, G., *Thermochim. Acta 145,* 19 (1989).
12. Skoršepa, J. S., Györyová, K., and Melník, M., *J. Therm. Anal. 44*, 169 (1995).
13. Jóna, E., Hvastijová, M., and Kohout, J., *J. Therm. Anal. 41*, 161 (1994).
14. D'Ascenzo, G., Ceipidor, U. B., Cardarelli, E., and Magri, A. D., *Thermochim. Acta 13*, 449 (1975).
15. Šramko, T., Liptay, G., and Jóna, E., *J. Therm. Anal. 12*, 217 (1977).
16. Masuda, Y., *Thermochim. Acta 39*, 235 (1980).
17. Mojumdar, S. C., Melník, M., and Jóna, E., *J. Anal. Appl. Pyrolysis 46*, 147 (1998).
18. Mojumdar, S. C., Melník, M., and Jóna, E., *Pol. J. Chem. 73*, 293 (1999).
19. Mojumdar, S. C., Valko, M., and Melník, M., *Chem. Pap. 52*, 650 (1998).
20. Mojumdar, S. C., Melník, M., Jóna, E., and Hudecová, D., *Chem. Pap. 53*, 265 (1999).
21. Mojumdar, S. C., Melník, M., and Jóna, E., *Chem. Pap. 53*, 309 (1999).
22. Mojumdar, S. C., Hudecová, D., Melník, M., and Jóna, E., *Chem. Pap. 54*, 39 (2000).
23. Mojumdar, S. C., Melník, M., and Jóna, E., *Thermochim. Acta 352*, 129 (2000).
24. Mojumdar, S. C. and Melník, M., *Chem. Pap. 54*, 1 (2000).
25. Mojumdar, S. C., *J. Therm. Anal. Cal. 64*, 629 (2001).
26. Mojumdar, S. C., Melník, M., and Jóna, E., *J. Therm. Anal. Cal. 56,* 533 (1999).
27. Mojumdar, S. C., Ondrejkovičová, I., Nevidanská, L., and Melník, M., *J. Anal. Appl. Pyrolysis*, in press.
28. Bleaney, B. and Bowers, K. D., *Proc. R. Soc. London A214*, 451 (1952).
29. Melník, M., Koman, M., Moncoľ, J., and Glowiak, T., *J. Coord. Chem. 53*, 173 (2001).
30. Melník, M., *Coord. Chem. Rev. 36*, 1 (1981).
31. Deveto, G., Ponticelli, G., and Preti, C., *J. Inorg. Nucl. Chem. 37*, 1635 (1975).
32. Kidani, Y., Noji, T., and Koike, H., *Bull. Chem. Soc. Jpn. 48*, 239 (1975).
33. Aslanian, D., Lautic, A., Mantai, Ch., and Baltanski, M., *J. Chim. Phys. 72*, 1052 (1957).
34. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 283. Wiley, New York, 1986.
35. Alcock, N. W., Tracy, V. M., and Waddington, T. C., *J. Chem. Soc., Dalton Trans. 1976*, 2243.