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REACTIONS OF RUTHENIUM(III), RHODIUM(III) AND IRIDIUM(III) CHLORIDES IN MOLTEN NITRITE EUTECTICS

S.S. AL OMER, K.A. ASKAR and D.A. HABBOUSH *

Department of Chemistry, College of Science, University of Basrah, Basrah (Iraq)

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ABSTRACT

The reactions of ruthenium(III), rhodium(III) and iridium(III) chlorides in molten lithium nitrite—sodium nitrite, lithium nitrite—potassium nitrite and sodium nitrite—potassium nitrite eutectics were studied and compared with those of their first row congeners. Ruthenium(III) reacted to form hexanitroruthenate(II) with the evolution of nitrogen dioxide, whereas rhodium(III) and iridium(III) formed hexanitrorhodate(III) and hexanitroiridate(III), respectively. These complexes decomposed at higher temperatures to form ruthenium(IV), rhodium(III) and iridium(IV) oxides, respectively, with the evolution of nitrogen oxides. The stoichiometries of these reactions were established by thermogravimetry and the products were characterized by their IR, visible and UV spectra, and X-ray diffraction patterns.

INTRODUCTION

The inorganic chemistry of transition metals in molten nitrites has revealed an interesting variety of chemical reactions. The published work reviewed here is mainly confined to first row transition series. Oxides and oxyanions of chromium(VI) [1—3], molybdenum(VI) and tungsten(VI) [4] behaved as Lux-Flood acids. Oxidation—reduction reactions were demonstrated by the oxidation of titanium metal [5] and of chromium(III) to chromate(VI) [3], and by the reduction of silver(I) to metallic silver [6] and of vanadium(V) to vanadium(IV) [7]. Manganate(V) [8], ferrate(V) and cobaltate (V) [9] were stabilized in molten nitrite solutions of sodium peroxide. In molten sodium nitrite-potassium nitrite iron(III), nickel(II) and copper(II) behaved as acids, whereas iron(II) and cobalt(II) suffered oxidations followed by acid—base reactions [10,11]. In the lower melting lithium nitrite—potassium nitrite, however, cobalt(II) and cobalt(III) formed insoluble hexanitrocobaltate(III), whereas nickel(II) and copper(II) formed soluble complexes containing both nitro and nitrito ligands [12]. In a more recent study [13], palladium(II), platinum(II) and platinum(IV) were reported to form soluble nitro and nitrito coordinated palladium(II) and

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* Present address: Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, U.S.A.

platinum(II) complexes which reacted further producing palladium and platinum metals, respectively.

In view of the possibility of coordination and the formation of nitrito/nitro complexes of transition metals in molten nitrites, the reactions of ruthenium(III), rhodium(III) and iridium(III) chlorides in these melts have been systematically investigated and the results are reported. Their reactions were compared with those of their first row congeners.

EXPERIMENTAL

Materials

Anhydrous ruthenium(III) chloride (Merck), rhodium(III) chloride and iridium(III) chloride (Fluka) were used as received. Analar sodium nitrite (Hopkin and Williams) and pure potassium nitrite (Riedel-de Haen) were dried at 150°C. Lithium nitrite was prepared by a previously reported method [14], and dried under reduced pressure at 110°C. Lithium nitrite—sodium nitrite [13], lithium nitrite—potassium nitrite [12] and sodium nitrite—potassium nitrite [3] were prepared as previously described.

Analysis

Nitrate, in the presence of nitrite, was estimated spectrophotometrically [15]. Other analyses were performed by Analytische Laboratorien, Elbach, Germany.

Procedure

Thermogravimetric studies were carried out under nitrogen atmosphere, using 0.5 g of the nitrite eutectics in vitroecil crucibles, on a Stanton-Redcroft MF-H5 massflow thermobalance, with a heating rate of 5°C min^{-1}, but kept isothermal at temperatures 20°C below the initial decomposition temperatures of the melts. (The initial decomposition temperatures of the lithium nitrite—sodium nitrite, lithium nitrite—potassium nitrite and sodium nitrite—potassium nitrite are 420, 450 and 550°C, respectively [13]). Weight losses were corrected for nitrate formation by the reaction

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \qquad (1)$$

Infrared spectra of the powdered products pressed into thin discs with potassium bromide and of gaseous products were measured, for the 4000—400 cm^{-1} region, on a Perkin-Elmer 377 spectrometer. Visible and UV spectra of aqueous solutions were taken on a Pye-Unicam SP1800 spectrophotometer. The X-ray powder patterns were obtained on a Philips 1410 diffractometer using nickel filtered CuK_α radiation.

RESULTS AND DISCUSSION

The black crystals of ruthenium(III) chloride were insoluble and stable in the lithium nitrite—potassium nitrite eutectic up to 250° C, after which they commenced to react slowly, forming a yellow precipitate and evolving brown fumes of nitrogen dioxide only. At 350° C the precipitate reacted to produce a black residue and evolving nitric and nitrous oxides. The powder pattern of the washed and dried residue ["*d*" values 3.17(100), 2.55(88), 2.24(13), 1.69(35) and 1.59(9) Å], corresponded to that of ruthenium(IV) oxide [A.S.T.M. index 3.17(100), 2.55(50), 2.24(10), 1.69(30) and 1.59(9) Å]. Analysis of the washed and dried yellow precipitate gave the following: K, 28.3 ± 0.1; Ru, 18.6 ± 1.2; N, 12.7 ± 1.8% (calculated for $K_4Ru(NO_2)_6$: K, 29.3; Ru, 18.9; N, 15.8%). Its IR spectrum, referred to as the ruthenium complex (Table 1), and the visible and UV spectra of its aqueous solution (Table 2), were comparable to those of potassium barium and potassium lead hexanitroferrate(II) [16,17]. Its powder pattern is given in Table 3; potassium hexanitroruthenate(II) is not reported in the A.S.T.M. index. Thermogravimetry of ruthenium(III) chloride (Fig. 1, curves A, B and C) showed two stages of weight loss in all the three nitrite melts, commencing at 200, 230 and 260° C, with overall weight losses of 61.7, 53.6 and 51.8%, respectively (calculated for loss of 3 N + 4 O per $RuCl_3$ is 51.1%). Weight losses at the end of the first stage averaged 21.2, 20.2 and 19.0%, respectively (calculated for loss of 1 N + 2 O per $RuCl_3$ is 22.2%).

Thermograms of the ruthenium complex, separated from the lithium nitrite—potassium nitrite melt, in all the three nitrite melts (Fig. 1, curves D, E and F) were similar to the second stage of those of the ruthenium(III)

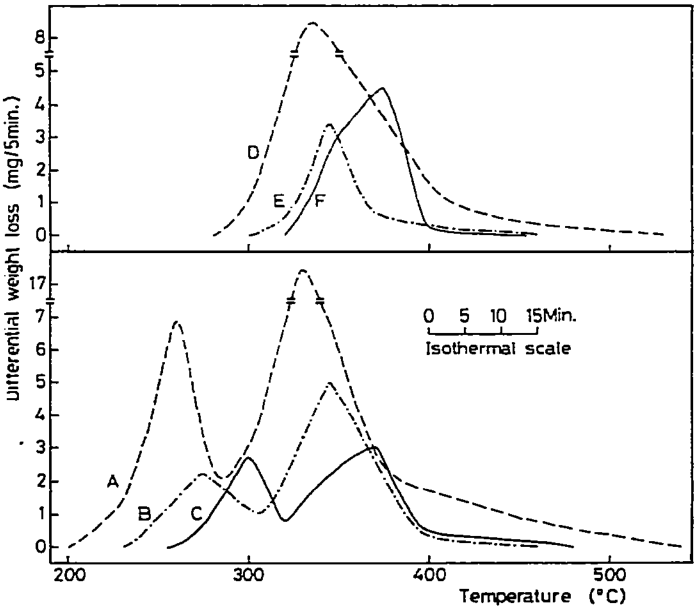

Fig. 1. Thermogravimetry of $RuCl_3$: A, 0.63 m in $LiNO_2$—$NaNO_2$; B, 0.21 m in $LiNO_2$—KNO_2; C, 0.22 m in $NaNO_2$—KNO_2. Thermogravimetry of Ru complex: D, 0.35 m in $LiNO_2$—$NaNO_2$; E, 0.09 m in $LiNO_2$—KNO_2; F, 0.27 m in $NaNO_2$—KNO_2.

TABLE 1

Infrared spectra (cm^{-1}) of complexes from reactions in molten lithium nitrite—potassium nitrite eutectic

	$\nu_a(NO_2)$		$\nu_s(NO_2)$			$\delta(ONO)$	$\rho_w(ONO)$	Ref.
Ruthenium complex	1625 w		1327 vs	1290 vs	1170 m	817 s	650, 605 w	
$K_2BaFe(NO_2)_6$	1630 vw		1332 vs		1184 m	820 s	644, 607 w	16
$K_2PbFe(NO_2)_6$	1637 vw	1565 vw	1320 vs	1300 vs	1190 m	830 s	645 w	16
Rhodium complex	1385 s		1337 s			825 s	628 m	
$K_3Rh(NO_2)_6$	1390 s		1340 s			833 s	627 m	19
Iridium complex	1385 s, br		1338 s			826 s	657 m	
$K_3Ir(NO_2)_6$	1390, 1375 s		1330 s			830 s	657 m	19

TABLE 2

Visible and UV spectra (kK) of aqueous solutions of complexes from reactions in molten lithium nitrite—potassium nitrite eutectic

Ruthenium complex	48.1 vs	36.5 s, sh, tailed to 20.2				
$K_2BaFe(NO_2)_6$ *	50.0	40.8	31.0	24.4	20.0	Ref. 17
$K_2BaFe(NO_2)_6$ **		37.04	31.65	26.64	22.22 sh	Ref. 16
$K_2PbFe(NO_2)_6$ **		38.77	30.3 sh	25.5	20.83	Ref. 16
Rhodium complex	49.0 vs	37.0 s	29.85 sh, tailed to 25.0			
$K_3Rh(NO_2)_6$	50.0 vs	37.0 s	29.8 sh			Ref. 20
Iridium complex	50.25 vs	38.1 s, sh	30.75 sh, tailed to 25.0			

* Spectra in KCl pellets.
** Reflectance spectra.

TABLE 3

Powder pattern of complexes from reactions in molten lithium nitrite—potassium nitrite eutectic

Ru complex *		$K_3Co(NO_2)_6$ **		Rh complex		Ir complex		$K_3Ir(NO_2)_6$ ** †	
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
7.38	38	6.07	30	6.13	63	6.13	66		
6.22	55	5.26	35	5.31	65	5.31	71		
5.58	10	3.72	60	3.76	83	3.76	100		
4.21	9			3.21	20	3.21	58	3.19	70
3.75	44	3.04	25	3.07	8			3.06	60
3.66	35	2.63	100	2.66	100	2.66	95	2.65	80
3.34	7	2.41	14	2.44	5	2.44	18		
3.12	9	2.35	45	2.38	47	2.38	62	2.36	80
2.63	100	2.15	75	2.17	82	2.17	100	2.16	100
2.44	9	2.02	16	2.05	16	2.05	33	2.03	60
2.25	10	1.859	18	1.881	21	1.883	27	1.866	60
2.15	37			1.797	9	1.799	26	1.784	60
2.10	16			1.773	7	1.775	17	1.760	50
2.06	5	1.662	20	1.682	19	1.684	29	1.673	80
1.926	8			1.622	3	1.622	7	1.615	40
1.874	10			1.605	5	1.604	9	1.598	40
1.835	9			1.537	4	1.536	5	1.529	20
1.714	4			1.492	8	1.492	17	1.483	60
1.670	10	1.458	12	1.478	7	1.478	11	1.467	50
1.650	7	1.405	30	1.423	29	1.423	42	1.415	100
1.560	6			1.386	5	1.386	10	1.377	60
1.512	3	1.315	12	1.331	7	1.331	5	1.328	20
1.480	3			1.292	4			1.288	50
1.416	9			1.255	7			1.247	70
1.401	6	1.239	10	1.230	4			1.224	60
1.378	4			1.222	4			1.214	60
1.344	3	1.175	16	1.190	6			1.184	40
1.310	4								
1.277	3								
1.184	3								

* Plus nine very weak lines.
** A.S.T.M. index.
† Using Fe radiation.

chloride in corresponding melts. The overall weight losses were 17.6, 15.5 and 10.9%, respectively (calculated for loss of 2 N + 2 O per $K_4Ru(NO_2)_6$ is 11.2%).

The reaction of ruthenium(III) chloride thus proceeded via the initial reduction and complex formation reaction

$$RuCl_3 + 7\ NO_2^- \rightarrow Ru(NO_2)_6^{4-} + 3\ Cl^- + NO_2 \qquad (2)$$

followed by the decomposition reaction

$$Ru(NO_2)_6^{4-} \rightarrow RuO_2 + 4\ NO_2^- + 2\ NO \qquad (3)$$

The relatively high weight losses observed in lithium nitrite—sodium nitrite and lithium nitrite—potassium nitrite melts were attributed to decomposition of the melts, catalyzed by the presence of the heavy metal oxide. The decomposition of the nitrite melts would explain the presence of nitrous oxide [18] among the gaseous products of the reaction. Comparison of the reactions of ruthenium(III) chloride and iron(III) chloride [10] in the nitrite melts indicated a lower tendency of the former to form the oxide.

The red powder of rhodium(III) chloride was insoluble and unreactive in the lithium nitrite—potassium nitrite eutectic at 120° C. On gradually raising the temperature a pale yellow precipitate started to form slowly at 160° C and faster at 200° C. At 400° C the precipitate reacted to produce a black residue and evolved brown fumes which were shown by IR to consist of nitrogen dioxide, nitric oxide and nitrous oxide. The powder pattern of the

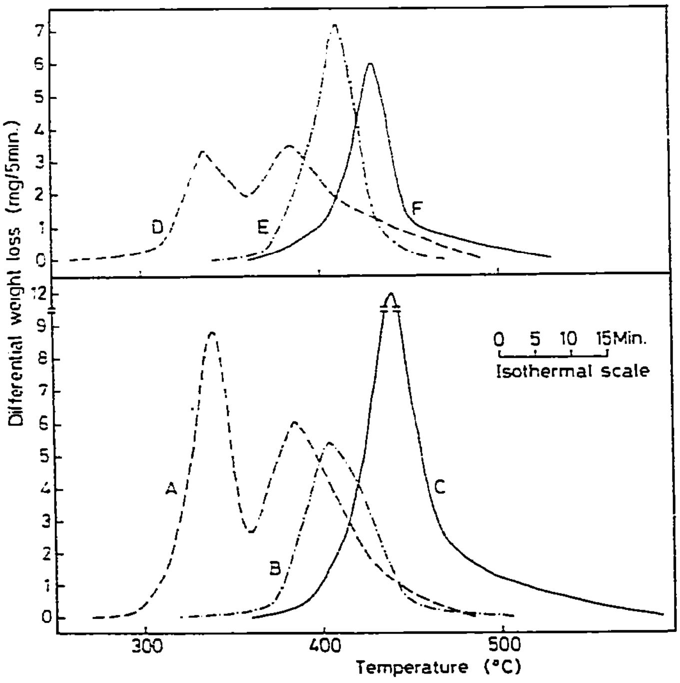

Fig. 2. Thermogravimetry of $RhCl_3$: A, 0.41 m in $LiNO_2$—$NaNO_2$; B, 0.14 m in $LiNO_2$—KNO_2; C, 0.42 m in $NaNO_2$—KNO_2. Thermogravimetry of Rh complex: D, 0.15 m in $LiNO_2$—$NaNO_2$; E, 0.24 m in $LiNO_2$—KNO_2; F, 0.17 m in $NaNO_2$—KNO_2.

washed and dried residue ["*d*" values 3.66(12), 2.64(100), 2.57(51), 1.53(40) and 1.33(11) Å] corresponded to that of rhodium(III) oxide [A.S.T.M. index 3.68(16), 2.63(100), 2.57(40), 1.50(35) and 1.31(6) Å]. The pale yellow precipitate, which showed only slight solubility in water, was separated from aqueous solutions of solidified melts by filtration and dried at 110°C. The IR spectrum of the precipitate, referred to as the rhodium complex (Table 1), and the visible and UV spectra of its aqueous solution (Table 2) were similar to those reported for potassium hexanitrorhodate(III) [19,20]. Its powder pattern (Table 3) can be compared to those of potassium hexanitrocobaltate(III) and potassium hexanitroiridate(III); potassium hexanitrorhodate(III) is not reported in the A.S.T.M. index. Thermogravimetry of rhodium(III) chloride in the three nitrite eutectics (Fig. 2, curves A, B and C) showed the reaction commencing at 270, 320 and 360°C, with overall weight losses of 56.9, 53.6 and 53.9%, respectively (calculated for loss of 3 N + 4.5 O per $RhCl_3$ is 54.5%).

Thermogravimetry of the rhodium complex, separated from the lithium nitrite—potassium nitrite melt, in all the three melts (Fig. 2, curves D, E and F) showed similar thermograms to those of the rhodium(III) chloride in corresponding melts. The overall weight losses were 24.9, 22.5 and 21.7%, respectively (calculated for loss of 3 N + 4.5 O per $K_3Rh(NO_2)_6$ is 23.0%).

The reaction of rhodium(III) chloride in the nitrite melts thus proceeded via the initial complex formation

$$RhCl_3 + 6\ NO_2^- \rightarrow Rh(NO_2)_6^{3-} + 3\ Cl^- \qquad (4)$$

followed by the decomposition reaction

$$2\ Rh(NO_2)_6^{3-} \rightarrow Rh_2O_3 + 6\ NO_2^- + 3\ NO_2 + 3\ NO \qquad (5)$$

The black crystals of iridium(III) chloride reacted slowly in the lithium nitrite—potassium nitrite eutectic at 140°C and faster at 170°C, forming a white precipitate with the liberation of a very small amount of nitric oxide which, although not detectable by thermogravimetry, was recognized by its IR band [21] at 1875 cm^{-1}. At 420°C the white precipitate reacted to produce a black residue and evolved nitrogen dioxide, nitric oxide and nitrous oxide. The powder pattern of the washed and dried residue ["*d*" values 3.18(79), 2.58(100), 2.25(24), 1.70(73) and 1.41(22) Å] corresponded to that of iridium(IV) oxide [A.S.T.M. Index 3.18(100), 2.58(90), 2.25(25), 1.70(55), and 1.41(14) Å]. The IR spectrum (Table 1) and the powder pattern (Table 3) of the washed and dried white precipitate, referred to as the iridium complex, corresponded to those of potassium hexanitroiridate(III) [19]. Visible and UV spectra of its aqueous solution (Table 2) revealed three charge transfer bands similar to those of potassium hexanitrorhodate(III) [20]. Thermogravimetry of iridium(III) chloride in the three nitrite eutectics (Fig. 3, curves A, B and C) showed the reaction commencing at 300, 360 and 400°C, with overall weight losses of 34.9, 34.7 and 35.3%, respectively (calculated for loss of 3 N + 4 O per $IrCl_3$ is 35.5%).

Thermograms of the iridium complex in all the three melts (Fig. 3, curves D, E and F) were similar to those of the iridium(III) chloride in corresponding melts. The overall weight losses were 20.0, 19.2 and 18.2%, respectively

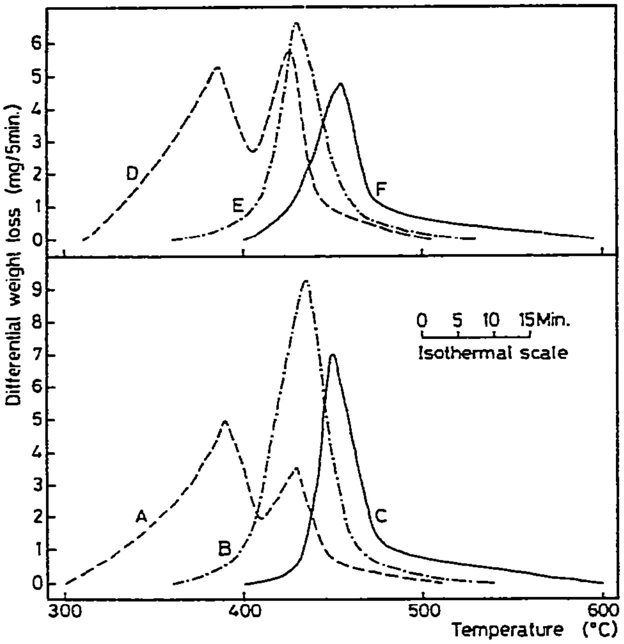

Fig. 3. Thermogravimetry of $IrCl_3$: A, 0.22 m in $LiNO_2$—$NaNO_2$; B, 0.34 m in $LiNO_2$—KNO_2; C, 0.25 m in $NaNO_2$—KNO_2. Thermogravimetry of Ir complex: D, 0.25 m in $LiNO_2$—$NaNO_2$; E, 0.16 m in $LiNO_2$—KNO_2; F, 0.13 m in $NaNO_2$—KNO_2.

(calculated for loss of 3 N + 4 O per $K_3Ir(NO_2)_6$ is 18.1%).

Thus, the reaction of iridium(III) chloride in the nitrite melts proceeded via the initial complex formation

$$IrCl_3 + 6\ NO_2^- \rightarrow Ir(NO_2)_6^{3-} + 3\ Cl^- \qquad (6)$$

followed by the decomposition

$$Ir(NO_2)_6^{3-} \rightarrow IrO_2 + 3\ NO_2^- + NO_2 + 2\ NO \qquad (7)$$

The liberation of small amounts of nitric oxide during the formation of the complex was attributed to the presence of traces of impurities, such as iridium(IV), which may have reacted according to the reaction

$$Ir^{4+} + 8\ NO_2^- \rightarrow Ir(NO_2)_6^{3-} + NO_3^- + NO \qquad (8)$$

Although, the lithium nitrite—sodium nitrite thermograms for both rhodium (Fig. 1, curves A and D) and iridium (Fig. 2, curves A and D) showed two stages of weight loss, attempts to separate intermediates at the end of the first stage were unsuccessful. The formation of hexanitrorhodate(III) and hexanitroiridate(III) is analogous to the formation of hexanitrocobaltate(III) in molten nitrite [12]. Comparison of the decompositions of these complexes in corresponding melts showed the expected trend of thermal stability: iridium > rhodium > cobalt. A similar trend of stability may also be expected for complexes of iron and its congeners, by comparison between the reaction of ruthenium(III) chloride with that of iron(III) chloride [10]. Although no differences have been observed, as far as the reaction products are concerned, between the three nitrite melts, cationic effect can easily be

recognized from the initial reaction temperatures and temperatures of maximum weight losses. This effect is consistent with changes in the polarizing power of the cations present in these melts.

REFERENCES

1 R.F. Bartholomew and D.W. Donigan, J. Phys. Chem., 72 (1968) 3545.
2 R.N. Kust and R.W. Fletcher, Inorg. Chem., 8 (1969) 687.
3 D.H. Kerridge and S.A. Tariq, Inorg. Chim. Acta, 3 (1969) 667.
4 S.S. Al Omer and D.H. Kerridge, Thermochim. Acta, 24 (1977) 97.
5 K. Hirata, N. Yoneyama and H. Tamura, Electrochim. Acta, 17 (1972) 793.
6 D.H. Kerridge and S.A. Tariq, Inorg. Chim. Acta, 4 (1970) 452.
7 S.S. Al Omer and D.H. Kerridge, Inorg. Chim. Acta, 7 (1973) 665.
8 R.B. Temple and G.W. Thickett, Aust. J. Chem., 25 (1972) 655.
9 R.B. Temple and G.W. Thickett, Aust. J. Chem., 26 (1973) 1137.
10 D.H. Kerridge and S.A. Tariq, Inorg. Chim. Acta, 4 (1970) 499.
11 S.A. Tariq, Chem. Ind., (1972) 122.
12 S.S. Al Omer and D.H. Kerridge, J. Chem. Soc., Dalton Trans., 11 (1978) 1589.
13 N.I. Al Salim, M.Sc. Thesis, University of Basrah, 1978.
14 W.C. Ball and H.H. Abram, J. Chem. Soc., 2 (1913) 2130.
15 Annual Book of A.S.T.M. Standards, Part 31 (1977) 422.
16 H. Elliott, B.J. Hathaway and R.C. Slade, Inorg. Chem., 5 (1966) 669.
17 K.G. Caulton and R.F. Fenske, Inorg. Chem., 6 (1967) 562.
18 A.K.K. Lee and E.F. Johnson, Inorg. Chem., 11 (1972) 782.
19 M. Le Postolloe, J.P. Mathiew and H. Poulet, J. Chim. Phys., 60 (1963) 1319.
20 H.H. Schmidtke, Z. Phys. Chem., 40 (1964) 96.
21 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York, 3rd edn., 1977.