Journal of Organometallic Chemistry, 238 (1982) 177—183
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

HALIDE AND COMPLEX HALOGENO ANIONS AS SALTS OF OXINATE CHELATES OF TITANIUM(IV) *

G.S. SODHI, A.K. SHARMA and N.K. KAUSHIK **

Department of Chemistry, University of Delhi, Delhi-7 (India)

(Received April 14th, 1982)

Summary

(η^5-Cyclopentadienyl)(η^5-pyrrolyl)titanium(IV) dichloride, (η^5-indenyl)(η^5-pyrrolyl)titanium(IV) dichloride and (η^5-cyclopentadienyl)(η^5-indenyl)titanium(IV) dichloride, when treated with 8-hydroxyquinoline (oxine) in aqueous medium form ionic derivatives of the type, $[(\eta^5\text{-R})(\eta^5\text{-R}')\text{TiL}]^+\ \text{Cl}^-$ ($R = C_5H_5$, C_9H_7, $R' = C_4H_4N$; $R = C_5H_5$, $R' = C_9H_7$; L is the conjugate base of oxine). A number of halide and complex halogeno anions present in aqueous solution were isolated as salts of these ionic complexes giving derivatives of the type, $[(\eta^5\text{-R})(\eta^5\text{-R}')\text{TiL}]^+\ X^-$ ($X = Br^-$, I^-, $ZnCl_3(H_2O)^-$, $CdCl_4^{2-}$, $HgCl_3^-$). Conductivity measurements in nitrobenzene solution indicate that these complexes are electrolytes. Both the IR and ^1H NMR spectral studies demonstrate that the ligand L is chelating. Consequently there is tetrahedral coordination about the titanium(IV) ion.

Introduction

Doyle and Tobias [1] pointed out that coordination of four oxygen atoms by strong covalent bonds to the $(\eta^5\text{-}C_5H_5)_2M^{IV2+}$ moiety (M = Ti, V) would lead to weakening of the metal—ring bonds. In order to investigate whether or not the coordination of two nitrogen and two oxygen atoms would produce a similar weakening of metal—ring bonds we studied the interaction of $(\eta^5\text{-R})(\eta^5\text{-R}')\text{TiCl}_2$ ($R = C_5H_5$, C_9H_7, $R' = C_4H_4N$; $R = C_5H_5$, $R' = C_9H_7$) with oxine in aqueous medium. We failed to isolate a derivative in which two oxinate groups coordinate to the $(\eta^5\text{-R})(\eta^5\text{-R}')\text{Ti}^{IV2+}$ moiety. However, ionic complexes of the type $[(\eta^5\text{-R})(\eta^5\text{-R}')\text{TiL}]^+\ \text{Cl}^-$ (L is the conjugate base of oxine), in which only one bidentate oxinate ligand is coordinated to the titanium(IV) ion were readily obtained. Such complexes possess low solvation energies as is evident from the

---

* From Ph.D. Thesis of G.S.S.

** Author for correspondence.

0022-328X/82/0000—0000/$02.75

ease of their preparation. This suggests that a number of halogeno anions present in aqueous solution might be isolated as salts of these complexes. The present communication describes the preparation and characterisation of such complexes.

Experimental

Nitrobenzene was purified for conductance measurements by the method described by Fay et al. [2]. Conductance measurements were made on an Elico Conductivity Bridge (Model CM-82). Magnetic measurements at room temperature were measured on a standard Gouy balance. Mercury tetrathiocyanatocobaltate(II) ($\chi_g = 16.44 \times 10^{-6}$ cgs units) was used as calibrant. Solid state IR spectra were recorded in KBr pellets in the 4000—200 cm^{-1} using a Perkin—Elmer 621 grating spectrophotometer. Visible spectra were recorded on an SF Russian recording spectrophotometer. ^1H NMR spectra were recorded at a sweep width of 900 Hz with a Perkin—Elmer R32 spectrometer. Chemical shifts are expressed relative to an internal reference of TMS (1% by volume).

Thallium(I) cyclopentadienide [3], thallium(I) indenide [4], sodium pyrrolide [5] and $(\eta^5\text{-}C_5H_5)TiCl_3$ [6] were synthesised by standard methods. $(\eta^5\text{-}C_9H_7)TiCl_3$ was prepared by the reaction of 1/1 molar ratios of $TiCl_4$ and C_9H_7Tl in THF by a similar method as described for $(\eta^5\text{-}C_9H_7)ZrCl_3$ by us [7].

Preparation of (η⁵-cyclopentadienyl)(η⁵-indenyl)titanium(IV) dichloride

To a rapidly stirred solution of 11.0 g (0.05 mol) $(\eta^5\text{-}C_5H_5)TiCl_3$ in 100 ml THF, a solution containing 16.0 g (0.05 mol) thallium(I) indenide in 150 ml THF was slowly added, with stirring. After the addition was complete, the contents were refluxed for about 4 h. The solution was filtered hot through a G4 filtration disk. The filtrate was concentrated under vacuum at room temperature. Petroleum ether was added to the concentrated filtrate. Brown precipitates were obtained, which were filtered, washed with petroleum ether and dilute hydrochloric acid. The product was recrystallised from an acetone solution by the addition of hexane. Colour, brown; yield, 50%; dec. temp., 183°C. Anal. Found: Cl, 23.81; Ti, 16.12. $C_{14}H_{12}Cl_2Ti$ calcd.: Cl, 23.75; Ti, 16.02%, IR (KBr): ν(Ti—Cl), 370; ν(C$\overset{...}{-}$H), 3050 cm^{-1}. ^1H NMR $(CD_3)_2CO$, δ 6.00 (s, 5H of cyclopentadienyl); 6.68—7.00 (m, 7H of indenyl) ppm.

Preparation of (η⁵-cyclopentadienyl)(η⁵-pyrrolyl)titanium(IV) dichloride

By following the series of steps described above, this compound was prepared by the reaction of 11.0 g (0.05 mol) $(\eta^5\text{-}C_5H_5)TiCl_3$ and 4.4 g (0.05 mol) sodium pyrrolide in THF. Colour, brown; yield, 55%; dec. temp., 185°C. Anal. Found: Cl, 28.53; N, 5.72; Ti, 19.28. $C_9H_9Cl_2NTi$ calcd.: Cl, 28.41; N, 5.60; Ti, 19.16%. IR (KBr): ν(Ti—Cl), 355; ν(C$\overset{...}{-}$N), 1445; ν(C$\overset{...}{-}$H), 3125 cm^{-1}. ^1H NMR $(CD_3)_2CO$, δ 5.94 (s, 5H of cyclopentadienyl); 6.70 (s, 2H, H α of pyrrolyl); 6.12 (s, 2H, H β of pyrrolyl) ppm.

Preparation of (η⁵-indenyl)(η⁵-pyrrolyl)titanium(IV) dichloride

This compound was prepared by the interaction of 13.4 g (0.05 mol) $(\eta^5\text{-}C_9H_7)TiCl_3$ and 4.4 g (0.05 mol) sodium pyrrolide in THF by the same procedure as given above. Colour, brown; yield, 50%; dec. temp., 220°C. Anal. Found: Cl, 23.57; N, 4.78; Ti, 15.86. $C_{13}H_{11}Cl_2NTi$ calcd.: Cl, 23.67; N, 4.66; Ti, 15.97%. IR (KBr): ν(Ti—Cl), 360; ν(C$\overset{...}{-}$N), 1445; ν(C$\overset{...}{-}$H), 3075 cm^{-1}. ^1H NMR $(CD_3)_2CO$: δ 6.15 (s, 2H, H β of pyrrolyl); 6.78—7.28 (m, 9H, H α of pyrrolyl and 7H of indenyl) ppm.

Preparation of halide and complex halogeno salts of titanium(IV) chelates

An aqueous solution of $[(\eta^5\text{-R})(\eta^5\text{-R}')TiL]^+ Cl^-$ ($R = C_6H_5, C_9H_7, R' = C_4H_4N$; $R = C_5H_5$; $R' = C_9H_7$; L = conjugate base of oxine) was obtained by stirring an aqueous solution of $(\eta^5\text{-R})(\eta^5\text{-R}')TiCl_2$ with a slight excess of solid oxine in about 100 ml double distilled water. After about 3 h, the contents were filtered and the aqueous solution was shaken with about 25 ml benzene. The aqueous phase was collected and added separately to an aqueous solution of KBr, KI, $ZnCl_2$, $CdCl_2$ or $HgCl_2$. The contents were warmed to 50°C and the resulting green precipitates of $[(\eta^5\text{-R})(\eta^5\text{-R}')TiL]^+ X^-$ ($X = Br^-, I^-, ZnCl_3(H_2O)^-, CdCl_4^{2-}, HgCl_3^-$) were filtered and washed with water followed by petroleum ether. These were reprecipitated from an acetone solution by the addition of petroleum ether.

Results and discussion

The method used for preparing and isolating $(\eta^5\text{-R})(\eta^5\text{-R}')TiCl_2$ complexes ($R = C_5H_5, C_9H_7, R' = C_4H_4N$; $R = C_5H_5, R' = C_9H_7$) yields materials of good purity as judged from satisfactory elemental analysis and spectroscopic data. The complexes are soluble in acetone, THF, DMSO and partially soluble in halogenated hydrocarbons. They are non-electrolytes as is evident from the conductance value of 0.5 ohm^{-1} cm^2 mol^{-1} for 0.5×10^{-3} *M* solutions of complexes in nitrobenzene. The electronic spectra of these compounds exhibit a single band in the 24700—24320 cm^{-1} region, which may be assigned to the charge transfer band, similar to that observed in case of complexes having the metal ions in $(n - 1)\, d^0ns^0$ configuration [8]. Magnetic susceptibility measurements at room temperature reveal that the compounds are diamagnetic.

Table 1 lists the analytical data and physical characteristics of the halogeno salts, $[(\eta^5\text{-R})(\eta^5\text{-R}')TiL]^+ X^-$ ($X = Br^-, I^-, ZnCl_3(H_2O)^-, CdCl_4^{2-}, HgCl_3^-$). These complexes are green in colour and thermally stable. They are soluble in acetone, THF and partially soluble in halogenated hydrocarbons. With $ZnCl_2$, an aquotrichloro zincate(II) anion is precipitated and coordinated water can be identified by intense infrared absorptions. Conductivity measurements reveal that all the complexes are 1/1 electrolytes in nitrobenzene. However in the case of cadmium(II) derivatives, the results are consistent with those of 1/2 electrolytes, indicating that dinegative anions are precipitated.

The infrared spectra of the $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ X^-$ and $[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ X^-$ complexes show a strong band at ~1460 cm^{-1} due to the vibrations of the C$\overset{...}{-}$N bond in the pyrrole ring. As the frequency of this band lies in between that for C—N and C=N bonds, it is evident that the C$\overset{...}{-}$N bond possesses partial double bond character. This band is absent in case of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ X^-$ derivatives.

The C$\overset{...}{-}$N band in the oxinate group shows a very intense absorption fre-

TABLE 1

PHYSICAL CHARACTERISTICS AND ANALYTICAL DATA

Complex [a]	Dec. temp. (°C) [b]	Conductance data Λ (ohm^{-1} cm^2 mol^{-1}) ($c = 1.5 \times 10^{-3}$ M)	Analyses (Found (Calcd.) (%))	
			Cl	N
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ Br^-$	176	28.8	—	3.16 (3.09)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ I^-$	195	30.2	—	2.72 (2.80)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ ZnCl_3(H_2O)^-$	132	26.4	18.90 (18.96)	2.55 (2.49)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]_2{}^+ CdCl_4{}^{2-}$	178	55.4	14.34 (14.22)	2.86 (2.80)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ HgCl_3$	100	29.2	15.78 (15.68)	2.11 (2.06)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ Br^-$	162	26.6	—	6.86 (6.95)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ I^-$	183	27.8	—	6.13 (6.22)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ ZnCl_3(H_2O)^-$	201	29.8	20.86 (20.77)	5.53 (5.46)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]_2{}^+ CdCl_4{}^{2-}$	199	55.8	15.63 (15.77)	6.29 (6.22)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ HgCl_3{}^-$	123	28.2	16.98 (16.90)	4.34 (4.44)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ Br^-$	148	28.6	—	6.25 (6.18)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ I^-$	161	28.8	—	6.68 (6.50)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ ZnCl_3(H_2O)^-$	120	29.2	18.81 (18.92)	5.05 (4.97)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]_2{}^+ CdCl_4{}^{2-}$	280	56.2	14.26 (14.19)	5.50 (5.59)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ HgCl_3{}^-$	150	26.8	15.78 (15.66)	4.19 (4.11)

[a] L = conjugate base of oxine (C_9H_6NO). [b] Uncorrected values.

quency at ~1330 cm^{-1}. Since this bond also possesses a partial double bond, similar to the $C\overset{\cdots}{-}N$ bond in the pyrrolyl group, it is expected that its vibrational frequency should occur in the 1450—1500 cm^{-1} range. In fact free oxine shows an intense absorption in this region. The occurrence of this band at lower energy in the present complexes indicates considerably less double bond character of the $C\overset{\cdots}{-}N$ bond in the oxinate group. It may be assumed that the lone pair of electrons on nitrogen is involved in the formation of a coordinate bond with the metal ion, which causes a drift of ring electrons towards nitrogen, making the double bond formation of the $C\overset{\cdots}{-}N$ bond considerably less as compared to that in free oxine. The presence of an intense band at ~1320 cm^{-1}, thus indicate that the oxinate ligand is chelating in all the complexes.

Magee and Gordan [9] studied the IR spectra of oxine and a number of metal oxinates. In the free oxine, they attributed the absorptions in the ~1500 cm^{-1} region to $\nu(C\overset{\cdots}{-}C)$ and $\nu(C\overset{\cdots}{-}N)$ stretching frequencies. No absorption frequency was observed at ~1320 cm^{-1} in this case. The IR spectra of the metal

TABLE 2

RELEVANT IR DATA [a] (cm^{-1}) (m, medium; s, strong; w, weak)

Complex	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	$\nu(\mathrm{M{-}Cl})$	$\nu(\mathrm{C{-}O})$ stretching	$\nu(\mathrm{C{-}H})$ in plane deformation	$\nu(\mathrm{C{-}H})$ out of plane deformation
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ Br^-$	(1335)(s)	—	1115(s)	1075(w) (1220)(m)	800(w), 825(m) 845(m), (785)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ I^-$	(1320)(s)	—	1110(s)	1080(w) (1225)(m)	805(w), 825(m) 840(w), (785)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ ZnCl_3(H_2O)^-$	(1335)(s)	330(w) 350(w)	1110(s)	1075(w) (1225)(m)	800(w), 850(m) (780)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]_2^+ CdCl_4^{2-}$	(1320)(s)	340(w) 375(m)	1105(s)	1085(w) (1220)(m)	810(w), 830(m), 845(m), (775)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)TiL]^+ HgCl_3^-$	(1325)(w)	325(w) 375(m)	1115(s)	1070(w) (1230)(m)	800(w), 850(m) (770)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ Br^-$	1450(m) (1330)(s)	—	1110(s)	1075(w) (1200)(m)	810(w), 825, 845(w), (785)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ I^-$	1460(m) (1335)(s)	—	1110(s)	1085(w) (1225)(m)	810(w), 850(s) (775)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ ZnCl_3(H_2O)^-$	1460(m) (1315)(s)	325(m) 365(m)	1105(s)	1070(w) (1215)(m)	805(w), 815(m) 855(w), (780)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ CdCl_4^{2-}$	1465(m) (1315)(s)	330(w) 370(m)	1115(s)	1075(w) (1220)(m)	800(w), 825(m), 850(w), (780)(m)
$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)TiL]^+ HgCl_3^-$	1460(m) (1325)(s)	335(w) 375(m)	1110(s)	1075(w) (1225)(m)	825(m), 850(m), (780)(m)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ Br^-$	1455(m) (1320)(s)	—	1105(m)	1075(w) (1210)(m)	825(m), 845(m) (780)(m)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ I^-$	1460(m) (1330)(s)	—	1115(m)	1085(w) (1200)(m)	800(w), 815(m), 850(w), (790)(m)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ ZnCl_3(H_2O)^-$	1455(m) (1335)(s)	325(m) 375(m)	1110(m)	1075(w) (1220)(m)	825(m), 845(w) (785)(m)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]_2^+ CdCl_4^{2-}$	1465(m) (1335)(s)	330(w) 380(m)	1110(m)	1090(w) (1215)(m)	800(w), 820(m), 850(w), (780)(m)
$[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ HgCl_3^-$	1460(m) (1330)(s)	320(w) 380(m)	1115(m)	1075(w) (1220)(m)	800(w), 830(m), 850(s), (785)(m)

---

[a] The values in parentheses are due to the oxinate group.

oxinates exhibited an absorption at ~1320 cm^{-1}. However, these authors did not give any explanation of this fact.

The complexes show medium intensity absorption bands in the 345—365 cm^{-1} region due to the metal—chlorine stretching vibrations [1,10]. No halide bridging is involved, since with the exceptions of bands assigned to the anions, the infrared spectra are virtually the same for all the complexes.

The $\nu(C\overset{...}{-}H)$ aromatic stretching frequency due to the π-ring systems and the oxinate group, result in broad absorption band at ~3000 cm^{-1}. The $\nu(C\overset{...}{-}C)$ aromatic stretching absorbs around 1435 cm^{-1}. The C—H out of plane deformation due to the π-ring systems result in weak to medium intensity bands in the 800—850 cm^{-1} region [1]. The C—H out of plane deformation due to the oxinate group occurs at ~750 cm^{-1} [9]. A weak band at ~1070 cm^{-1} is attributed to the C—H in plane deformation of the π-ring systems. This stretching frequency for the oxine absorbs at ~1220 cm^{-1} [9].

The in-plane oxine ring deformation shows an absorption at ~735 cm^{-1} [11]. The π-ring stretching frequencies result in an absorption at ~1360 cm^{-1} [1]. The C—O stretching frequency show an intense absorption centered around the 1115 cm^{-1} region [8]. A doublet is observed at 500 ± 30 cm^{-1}. The absorption at higher frequency is attributed to the C—O in plane bending [11] and that at lower frequency to M—O stretching vibrations. The characteristic IR frequencies together with their assignments are presented in Table 2.

The ^1H NMR spectra of the complexes were recorded in deuterated acetone. The C(2) proton of the oxinate group, in case of metal complexes, shows a signal at δ 9.10 ppm (q, J 4 and 1.6 Hz). This is downfield as compared to the value of δ 8.73 ppm for free oxine. Hence it supports the conclusion that the oxinate group is chelating. The signals due to the remaining protons of the oxinate group result in a complex multiplet in the range δ 7.4—8.2 ppm.

The signals due to the π-ring systems are in some cases shifted to lower fields as compared to those of the $(\eta^5\text{-R})(\eta^5\text{-R}')TiCl_2$ complexes. In the case of $[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_4H_4N)TiL]^+ X^-$ derivatives, the resonance signal arising as a result of α protons of the pyrrolyl group, overlap with that of indenyl protons. There is a lack of evidence of splitting between the α and β protons of the pyrrolyl group, similar to other pyrrolyl derivatives [12]. The spectra of the zinc(II) derivatives show an additional resonance signal (a broad peak at δ 4.18 ppm) due to the presence of a coordinated water molecule.

The possibility of oxinate ligand bonding by simple hard sphere coulombic interactions to $(\eta^5\text{-R})(\eta^5\text{-R}')Ti^{IV2+}$ moiety is ruled out because in such a case a bis-oxinate complex may be isolated. Such a structure would maximise the coordination number of the metal ion and simultaneously maximise the total metal-ring overlap. Since the π-clouds are used in the formation of metal—ring bonds and would exert less of a steric effect as the equatorial ligands, this configuration cannot be described as unstable on the basis of steric effects. However, applying Ballhausen and Dahl's theory [13] to the present complexes, it can be assumed that two strongly directed metal hybrids, which are used in $(\eta^5\text{-R})(\eta^5\text{-R}')TiCl_2$ are binding one oxinate ligands. Coordination of two oxygen and two nitrogen atoms in the *xy* plane by strong covalent bonds would result in the weakening of the metal-ring bonds and would be energetically unfavorable. The Ti—O and Ti—N bonds have appreciable covalent character, since only one oxinate ligand interacts.

Acknowledgement

We take this opportunity to thank the Council of Scientific and Industrial Research for awarding a Senior Research Fellowship to G.S.S. and A.K.S.

References

1 G. Doyle and R.S. Tobias, Inorg. Chem., 6 (1967) 1111; 7 (1968) 2484.
2 R.C. Fay and R.N. Lowry, Inorg. Chem., 6 (1967) 1512.
3 H. Meister, Angew. Chem., 69 (1957) 533.
4 K. Chandra, R.K. Sharma, A.K. Garg and B.S. Garg, Chem. Ind., (1980) 537.
5 K.K. Joshi, P.L. Pauson, A.R. Qazi and W.H. Stubbs, J. Organometal. Chem., 1 (1964) 471.
6 R.D. Gorsich, J. Am. Chem. Soc., 80 (1958) 4744.
7 G.S. Sodhi and N.K. Kaushik, Bull. Soc. Chim. France, 1-2 (1982) 45.
8 P.B. Dorain, H.H. Patterson and P.C. Jordan, J. Chem. Phys., 49 (1968) 3845.
9 R.J. Magee and L. Gordan, Talanta, 10 (1963) 851.
10 K. Chandra, R.K. Sharma, B.S. Garg and R.P. Singh, Transition Met. Chem., 4 (1979) 367.
11 J.E. Tackett and O.T. Sawyer, Inorg. Chem., 3 (1964) 692.
12 R.B. King and M.B. Bisnette, Inorg. Chem., 3 (1964) 796.
13 C.J. Ballhausen and J.P. Dahl, Acta Chem. Scand., 15 (1961) 1333.