Inorganica Chimica Acta, 142 (1988) 123–128

SO_3 Adducts of Hexameric Oxoniobate Cluster in Nonintegral Subnormal Oxidation States: Formation, Properties and Formulation

A. V. SAHA, P. BANDYOPADHYAY and B. K. SEN*

Department of Chemistry, University College of Science, 92, Acharya Prafulla Chandra Road, Calcutta-700009, India

(Received May 27, 1987)

Abstract

Niobium(V) in 9 M H_2SO_4 has been reduced by metallic zinc to a red–brown solution from which a series of salts containing the cluster anion, $[Nb_6O_7(O{\cdot}SO_3)_{12}]^{16-}$ have been isolated. The compounds have been characterized from analytical, IR spectral and magnetic data and the structure of the cluster and its formation are proposed. The anion is a 12-sulphur trioxide adduct of the 'Nb_6O_{19}' cluster and contains $Nb_6(22+)$ with the average valency of 3.67 for each Nb. $Nb_6(20+)$ corresponding to Nb(3.33) and $Nb_6(26+)$ corresponding to Nb(4.33) have been potentiometrically shown to be formed as redox derivatives of $Nb_6(22+)$ in different aqueous conditions. Isolation of solid Nb(3.33) has been attempted.

Introduction

Niobium(V) is known to form a polyoxoniobate cluster $Nb_6O_{19}^{8-}$ in aqueous phase and the structure of the anion has been established by X-ray crystallography [1] as well as ^{17}O NMR [2]. The present workers described [3] the corresponding isopolyniobic acid, $H_8Nb_6O_{19}{\cdot}xH_2O$ in the solid state and studied its thermal condensation at various temperatures using ^1H NMR. It has been shown [4, 5] that all the existing stoichiometric and nonstoichiometric oxides of niobium and the niobates are really the derivatives of the isopolyniobic acid, $H_8Nb_6O_{19}$, formed under various conditions. This isopolyniobic acid is, in fact, a protonated polyoxoniobate cluster. It is soluble in concentrated sulphuric acid and in solution niobium(V) exists as a hexanuclear species which is proposed [6] to be a SO_3 adduct of $H_8Nb_6O_{19}$. Thus the 'Nb_6O_{19}' cluster exists also in strong aqueous sulphuric acid medium. Such donor ability of $Nb_6O_{19}^{8-}$ was also established by Shimura *et al.* [7] as a cobalt(III) complex in which the cluster anion functions as a tridentate ligand.

It is now pertinent to examine if such a hexaniobium cluster also remains intact in the subnormal valency states of niobium and if it exists, in view of its electron-richness, how its coordinating ability varies. The reports of previous workers showed that niobium(V) in H_2SO_4 could be electrolytically reduced to species having a nonintegral valency state of 3.67. This fact readily suggests that the product is polynuclear in nature. Various workers isolated the reduced species in the form of different salts and free acids and have formulated them differently [8–11]. The present communication describes a detailed study of the sulphatoniobates in subnormal states of oxidation, in aqueous H_2SO_4 medium and proposes that the hexaniobate cluster exists as sulphur trioxide adduct of the polyoxoniobate cluster, $Nb_6O_{19}^{16-}$, with the metal atom having an average valency of 3.67. It is proposed that sulphur trioxide gets coordinated to the twelve bridging oxygen atoms of the $Nb_6O_{19}^{16-}$ cluster. New fractional valency states, Nb(2.33) and Nb(4.33), are reported as redox derivatives of hexanuclear Nb(3.67).

Experimental and Results

Pure niobium(V) oxide (Fluka) was used in the experiments and all other reagents were of appropriate purity. Magnetic measurements were made under nitrogen atmosphere by a Gouy balance at 298 K. Infrared spectra were recorded on a Beckman IR 20 spectrophotometer. For potentiometric measurements a Cambridge portable pH meter was used.

Preparations

Stock solutions of niobium(V) was made by fusing niobium(V) oxide (250 mg) with potassium pyrosulphate (3 g), extracting the cooled melt with 15 ml of hot concentrated sulphuric acid and diluting the cooled solution to 9 M acidity without allowing the temperature to rise beyond 0 °C. The solution was stored overnight in an ice-chest. 12 ml of this solution was reduced with 1 g of zinc dust to get a red–violet solution. After removing the excess

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

TABLE I. Data on Preparations

Compound[a]	Crude salt solution		Reagents				Yield (mg)
	Volume (ml)	H_2SO_4 concentration (M)	Salts	Weight (g)	H_2SO_4 concentration (M)	Volume (ml)	
$K_4Zn_4H_4[M]\cdot ZnSO_4\cdot 18H_2O$	50	9	$ZnSO_4\cdot 7H_2O$	3.0	6	19	115
			$KHSO_4$	2.0		solid	
$K_8H_8[M]\cdot 18H_2O$	80	6	$KHSO_4$	2.5		solid	440
$(NH_4)_8H_8[M]\cdot 12H_2O$	85	9	$(NH_4)_2SO_4$	5.0		solid	230
$Tl_8H_8[M]\cdot 12H_2O$	80	9	Tl_2SO_4	5.0	9	5	350
$K_6Co_2H_6[M]\cdot CoSO_4\cdot 18H_2O$	50	9	$CoSO_4\cdot 7H_2O$	2.0	6	8	150
			$KHSO_4$	3.0		solid	
$K_6MgH_8[M]\cdot 2MgSO_4\cdot 24H_2O$	70	9	$MgSO_4\cdot 7H_2O$	3.5	6	10	260
			$KHSO_4$	3.5		solid	
$K_7NiH_7[M]\cdot NiSO_4\cdot 24H_2O$	60	9	$NiSO_4\cdot 7H_2O$	2.5	6	10	200
			$KHSO_4$	2.0		solid	
$K_7Fe_{0.5}H_8[M]\cdot FeSO_4\cdot 24H_2O$	60	6	$FeSO_4\cdot 7H_2O$	2.0	6	16	200
			$KHSO_4$	3.0		solid	

[a] $M = Nb_6O_7(O\cdot SO_3)_{12}$.

of zinc, the solution was stirred with 200 mg of potassium hydrogen sulphate for 30 min under CO_2 and finally kept overnight in an ice-chest. The red–brown crystals thus obtained, were collected and washed quickly with a minimum volume of 6 M H_2SO_4. This crude crystalline product was used for the preparation of all the salts described, all operations being carried out in CO_2 atmosphere.

$K_4Zn_4H_4[Nb_6O_7(O\cdot SO_3)_{12}]\cdot ZnSO_4\cdot 18H_2O$: 3 g of zinc(II) sulphate heptahydrate and 2 g of $KHSO_4$, dissolved in 20 ml of 6 M H_2SO_4, were added to 50 ml of a saturated solution of the crude crystals in 9 M H_2SO_4. The mixture was stirred for an hour and then kept overnight at 25 °C to afford red–brown crystals. These were collected and washed with 2 ml portions of 6 M H_2SO_4 until free from excess of zinc and potassium sulphates, and finally washed free from sulphuric acid, with oxygen-free ethanol and acetone successively. It was dried under vacuum to yield 115 mg of the product.

Seven other salts were prepared by following more or less the same procedure as that for the potassium–zinc salt, the variation being in the concentration of sulphuric acid (depending on the solubilities of the reagents) and in the nature of reactants. Table I describes the conditions of preparations and the yields of all the products and Table II gives their analytical compositions. Niobium was determined gravimetrically as niobium(V) oxide, after oxidation and hydrolysis of the compounds in boiling 0.5 N H_2SO_4. Water content of the salts were determined from the loss in weight on isothermal heating of the compounds at 120 °C in dry nitrogen, while other constituents were determined in the conventional manner.

All the salts are soluble in water and insoluble in common organic solvents. The aqueous solution is unstable both due to hydrolysis and oxidation by atmospheric oxygen. The solid products are also oxidized slowly to white powder obviously to produce niobium(V).

Oxidation State of Niobium

The mean oxidation state of niobium in these compounds was determined by oxidizing freshly prepared products with known excess of standard cerium(IV) sulphate, followed by back titration with standard iron(II) sulphate. The niobium(V) in the resulting mixture was separated by its hydrolysis in boiling sulphuric acid medium (0.5 N) and determined gravimetrically. The mean experimental value was 3.69 ± 0.02, for all the salts, the formulas requiring 3.67.

Study of Oxidative Hydrolysis

The number of cations, other than H^+, associated with the anionic complex-unit was determined by the oxidative hydrolysis of the compounds followed by the determination of the liberated free acid.

$$M_m{}^{I}H_{16-m}[Nb_6O_7(O\cdot SO_3)_{12}]\cdot xH_2O - 8e \longrightarrow mM^+ + (32-m)H^+ + 3Nb_2O_5\cdot yH_2O + 12SO_4{}^{2-} + (x-y-8)H_2O$$

The equation shows that the liberated acid is related to m which was thus calculated from the experimental data. A known weight of the compound was treated with a known volume of standard aqueous sulphuric acid in the presence of atmospheric oxygen. The mixture was digested for two hours and the precipitated niobium(V) oxide was removed. The

TABLE II. Analytical, Oxidative-Hydrolysis and Magnetic Data

Compound[a]	Found (calc.) (%)					m (calc.)	μ_{eff} (BM)
	Nb	Alkali-metal/ NH_3	Other metal	S	H_2O		
$K_4Zn_4H_4[M]\cdot ZnSO_4\cdot 18H_2O$	20.8	5.1 (K)	12.0 (Zn)	15.1	11.9	11.2	0.43
	(20.4)	(5.7)	(12.0)	(15.2)	(11.9)	(12.0)	
$K_8H_8[M]\cdot 18H_2O$	23.1	12.6 (K)		15.6	12.6	8.2	1.10
	(22.6)	(12.7)		(15.6)	(13.1)	(8.0)	
$(NH_4)_8H_8[M]\cdot 12H_2O$	26.1	6.5 (NH_3)		16.7	9.3	8.0	1.40
	(25.5)	(6.3)		(17.5)	(9.9)	(8.0)	
$Tl_8H_8[M]\cdot 12H_2O$	15.0	43.1 (Tl)		11.1		8.5	
	(15.2)	(44.4)		(10.4)		(8.0)	
$K_6Co_2H_6[M]\cdot CoSO_4\cdot 18H_2O$	20.2	9.0 (K)	6.6 (Co)	15.4		10.8	8.00
	(20.9)	(8.8)	(6.6)	(15.6)		(10.0)	
$K_6MgH_8[M]\cdot 2MgSO_4\cdot 24H_2O$	20.1	8.7 (K)	2.5 (Mg)	15.6		8.0	1.10
	(20.2)	(8.5)	(2.6)	(16.2)		(8.0)	
$K_7NiH_7[M]\cdot NiSO_4\cdot 24H_2O$	20.3	10.3 (K)	4.2 (Ni)	14.7		9.1	4.80
	(20.3)	(9.9)	(4.3)	(15.1)		(9.0)	
$K_7Fe_{0.5}H_8[M]\cdot FeSO_4\cdot 24H_2O$	20.7	10.5 (K)	3.1 (Fe)	15.0		6.9	6.20
	(20.5)	(10.1)	(3.1)	(15.3)		(8.0)	

[a] $M = Nb_6O_7(O\cdot SO_3)_{12}$.

liberated excess acid in the filtrate was determined alkalimetrically using a suitable indicator (bromocresol green) so that the metal ions did not interfere in the acid base titration. The experimental values of m along with the theoretical values in parentheses are given in Table II.

Reduction of Nb(3.67) to Nb(3.33)

150 mg of pure $K_8H_8[Nb_6O_7(O\cdot SO_3)_{12}]\cdot 18H_2O$, dissolved in 15 ml of 6 M sulphuric acid, was reduced by 600 mg of zinc powder. The red–brown colour of the solution changed to dark green. It was filtered through a sintered glass bed to remove the excess unreacted zinc and the filtrate was directly treated with a known excess of standard cerium(IV) sulphate. All the operations were performed in nitrogen atmosphere. The excess cerium(IV) and the precipitated niobium(V) oxide were determined as before. The mean oxidation state of niobium, determined from a set of experiments, was 3.33 as also found by Golibersuch and Young [9]. It was observed that the oxidation state of niobium could never be reduced down to 3 by zinc under this condition.

Attempts to isolate the niobium(3.33) furnished a dark brownish green solid contaminated with H_2SO_4, with oxidation number, 3.40 and Nb:Zn:K, 1:0.36:0.44. The preparation was started with a concentrated solution of freshly precipitated niobic acid in 9 M H_2SO_4 reduced extremely with excess zinc and finally crystallized at 0 °C in the presence of saturated potassium hydrogen sulphate under nitrogen. The product could not be freed from H_2SO_4 due to its ready oxidizability to red Nb(3.67) salt.

Reaction of Niobium(3.67) with Aqueous Bicarbonate

In order to study the redox behaviour of niobium(3.67) at higher pH, aqueous bicarbonate buffer was selected as the proper medium, because both the niobium(V) and niobium(3.67) compounds were soluble in such a medium.

A weighed quantity of freshly prepared solid $K_8H_8[Nb_6O_7(O\cdot SO_3)_{12}]\cdot 18H_2O$ containing Nb(3.67) was added, with stirring, to saturated aqueous sodium bicarbonate containing a good excess of solid $NaHCO_3$, taken in a specially designed all-glass titration vessel. The titration assembly allowed completion of the experiment under a carbon dioxide atmosphere. During the addition of niobium compound, the mixture was stirred vigorously so that precipitation of hydrated niobium oxide due to the local increase of acidity of the solution could be avoided. The issuing gas was chased out by a stream of CO_2 and was collected in a micro gas-burette over 40% aqueous KOH. The volume of hydrogen gas, collected in the burette was measured. The resulting dark brown solution was titrated potentiometrically with standard iodine solution, using a polished platinum indicating electrode.

The experimental results indicated that niobium(3.67) was oxidized under these conditions to soluble Nb(4.33) with simultaneous liberation of 0.67 g atoms of hydrogen per mole of Nb(3.67) reacted. The formal potential of Nb(V)/Nb(4.33) system in saturated aqueous HCO_3^-/CO_2 medium, was measured to be −0.320 V *versus* SCE indicating the strong reducing nature of Nb(4.33).

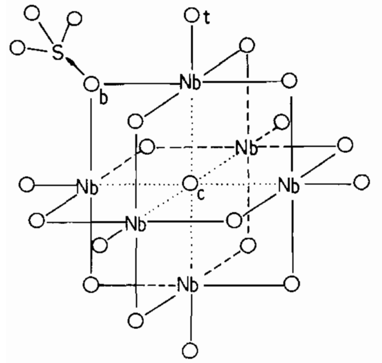

Fig. 1. Three types of oxide ions in $[Nb_6O_{19}]^{8-}$ and coordination O_b to SO_3.

Discussion

These lower valency niobium compounds are prepared by the reduction of niobium(V) in 9 M H_2SO_4 solution. It has been described earlier [6] that such a solution contains hexaniobium species which are regarded as the sulphur trioxido derivatives of isopolyniobic acid, $H_8Nb_6O_{19}$. The polyacid contains three types of oxide ions (Fig. 1), namely, one central (O_c), six terminal (O_t) and twelve bridging (O_b) oxide ions. SO_3 addition takes place at these bridging oxide ions and a maximum of dodecasulphurtrioxido derivative is thus possible. In the case of niobium(V), the tetrasulphurtrioxido derivative could be isolated in the solid state. It has been argued that, niobium(V) being strongly acidic, electron pair donation by the Nb–O–Nb becomes increasingly difficult, as more and more SO_3 groups are attached to $H_8Nb_6O_{19}$. As a result, this isopolyniobic acid unit does not usually add more than four SO_3 groups per hexamer. The situation changes with the reduction of the oxidation state of niobium, whereby the acidic property of the metal ions decreases and electron availability for coordination increases. Under this condition, a greater number of SO_3 groups could remain attached to the hexamer, reaching a maximum value at twelve. It is, however, tacitly assumed that, during reduction of niobium(V), the hexaniobium cluster is not broken open. The assumption is not, in any way, arbitrary since the mean oxidation number of 3.67 requires the compounds to be polymeric and at least, trinuclear in composition. The formation of the Nb(3.67) derivative can, thus, be represented by an eight-electron reduction of the hexamer

$$[Nb_6O_7(O{\cdot}SO_3)_xO_{12-x}]^{8-} + (12-x)H_2SO_4 + 8e \longrightarrow [Nb_6O_7(O{\cdot}SO_3)_{12}]^{16-} + (12-x)H_2O$$

The presence of $\begin{smallmatrix}Nb\\Nb\end{smallmatrix}\!\!>\!O \rightarrow SO_3$ grouping in these compounds, has been clearly established from their IR spectra (Table III). The coordination of an SO_3 group to an oxide ion, as depicted above, is analogous to a fluorosulphonate anion (FSO_3^-) where the fluoride ion replaces an oxide ion which is different from the three oxide ions of the O–SO_3 grouping. This distinctive oxygen is the bridging oxide ion (O_b) of the isopolyniobic acid hexamer. The effective difference between this 'O–SO_3' and a normal 'SO_4' group is the change of its symmetry to C_{3v} from the T_d of the latter. This would lead, firstly, to the enhancement of the absorption of the totally symmetric S–O stretching mode, ν_1 and secondly,

TABLE III. IR Spectral Data[a]

Compound[b]	Vibration frequencies of 'O–SO_3' group (cm^{-1})[c]			Other vibrations (cm^{-1})
	ν_1	ν_3	ν_4	
$K_4Zn_4H_4[M]{\cdot}ZnSO_4{\cdot}18H_2O$	990(s)	1140(s), 1230(s)	670(m), 610(m)	3560–3400(bs), 1640(m), 870(vw), 780(vw), 730(vw)
$K_8H_8[M]{\cdot}18H_2O$	970(s)	1110(s), 1220(s)	645(sh)	3500–3200(bs), 2300(w), 1620(m), 1500(w)
$(NH_4)_8H_8[M]{\cdot}12H_2O$	970(s)	1120(s), 1215(s)	655(m), 610(m)	3200–3100(bs), 1620(w), 1395(s), 1040(vw)
$K_6Co_2H_6[M]{\cdot}CoSO_4{\cdot}18H_2O$	980(s)	1130(s), 1220(s)	650(sh), 600(m)	3480–3380(bs), 1640(m), 1170(sh), 845(m)
$K_6MgH_8[M]{\cdot}2MgSO_4{\cdot}24H_2O$	980(s)	1120(s), 1220(s)	650(m)	3480–3360(bs), 1660(m), 960(sh), 890(vw), 840(vw)
$K_7NiH_7[M]{\cdot}NiSO_4{\cdot}24H_2O$	970(s)	1110(s), 1220(s)	650(m), 610(sh)	3500–3200(bs), 1660–1630(m), 955(sh), 840(vw)
$K_7Fe_{0.5}H_8[M]{\cdot}FeSO_4{\cdot}24H_2O$	990(s)	1135(s), 1240(s)	665(m), 620(sh)	3460–3400(bs), 1650(m), 1320(sh), 840(vw)

[a] s = strong; bs = broad strong; m = medium; w = weak; v = very; sh = shoulder. [b] M = $Nb_6O_7(O{\cdot}SO_3)_{12}$. [c] ν_2 could not be recorded.

the splitting of the triply degenerate S–O stretching mode of the T_d ion, ν_3 and ν_4, into two IR active bands of A_1 and E type. The magnitude of the splitting of ν_3 and ν_4 would determine the extent of departure of the distorted '$O{-}SO_3$' group from the symmetric SO_4^{2-} ion. The analysis of the IR spectral bands (Table III) clearly establishes that the '$O{-}SO_3$' group really exists in these compounds. The magnitude of the splitting of the ν_3 bands (90–110 cm^{-1}) is much higher than that of monodentate sulphate ligands (50–60 cm^{-1}) [12–14] and nearer to that of FSO_3^- (160 cm^{-1}) [15]. This feature clearly shows that the distinctive oxygen (O_b) of '$O{-}SO_3$' belongs more to the oxoniobium system than to the SO_3 system. The same conclusion can be reached from the absolute positions of the ν_3 bands in the niobium compounds, which are closer to the bands [15] of FSO_3^- and much higher to those in the spectra of unidentate sulphato complexes [12–14].

The hexanuclear niobium(V) compounds possess 30 units of positive charge per niobium hexamer. This could be, in principle, reduced gradually to 18 units when all the niobium ions in the hexamer would be in the tripositive states. Further reduction is only possible when the oxidation state of niobium is decreased below 3 which is not encountered in an aqueous environment. All the intermediate positive charges of the hexaniobium cluster between 18 and 30 should be obtained in principle. In aqueous H_2SO_4 only two intermediate species $Nb_6(22+)$ and $Nb_6(20+)$ corresponding to Nb(3.67) and Nb(3.33) have been obtained. In aqueous bicarbonate, another species containing $Nb_6(26+)$ corresponding to Nb(4.33) has also been obtained. No other intermediate species has so far been prepared. It is not known if these positive charges are localized on specific niobium ions in the cluster or are delocalized throughout by metal–metal bonding. In any case, these different species prove the existence of polymeric systems.

The susceptibility measurements with the freshly prepared red–brown compounds under nitrogen atmosphere show that the effective magnetic moment (Table II) of the salts containing diamagnetic cations, is *ca.* 1 BM per 'Nb_6' unit. This very low paramagnetism is not commensurate with localized electrons and indicates the possible Nb–Nb interaction in the cluster as described earlier [6].

An important feature of all the salts is their large stoichiometric water content. The bindings of these water molecules in the $K{-}M^{II}$ salts (M^{II} = Zn, Mg, Ni, Co, Fe) are complicated due to interplay of two factors, *viz.*, coordination and hydrogen bonding. Niobium being coordinately saturated in the cluster, coordination only occurs at the M^{II} ions while it is absent in M^I salts (M^I = K, Tl, NH_4). In the latter compounds, the degree of hydration is found to be maximum for the potassium salt and this can be accounted for in a manner analogous to the isopolyniobic acid hydrates [4]. In the $H_8[Nb_6O_7(O{\cdot}SO_3)_{12}]^{8-}$ anion, the six terminal niobyl oxygens (O_t) are deep-seated compared to the 36 peripheral oxygen atoms of 12 coordinated SO_3 groups. These 36 oxygen atoms, being more exposed outwardly, will be able to bind a maximum of 18 water molecules using both the hydrogen atoms for hydrogen bonding and this makes the potassium salt an 18-hydrate. Presence of such hydrogen bonded lattice water is indicated by the broad O–H stretching bands (*ca.* 3500–3200 cm^{-1}) in the IR spectra. The lesser degree of hydration ($12H_2O$) in ammonium and Tl(I) salts may be due to the protic NH_4^+ and large Tl^+ ions, which partially affect hydrogen bonding in the anionic structure.

The red–brown $Nb_6(22+)$ is reduced by metallic zinc up to green $Nb_6(20+)$ which was stable both in solution and in the solid state provided that excess of free sulphuric acid was present. It is easily oxidized back to $Nb_6(22+)$ showing once again the comparable stability of the latter state. The fractional valency of 3.33 for each niobium atom clearly fits with a 2-electron reduction of the hexaniobium cluster as

$$[Nb_6O_7(O{\cdot}SO_3)_{12}]^{16-} \xrightarrow{+2e} [Nb_6O_7(O{\cdot}SO_3)_{12}]^{18-}$$

and the brownish green solid is, obviously, the salt of this reduced anion.

The instantaneous conversion of $Nb_6(22+)$ to $Nb_6(26+)$ in aqueous bicarbonate, indicates the great instability of the former at higher pH. The $Nb_6(26+)$ is oxidizable to $Nb_6(30+)$, *i.e.* Nb(V), by iodine. Assuming that the hexaniobium cluster remains unchanged, the oxidation of $Nb_6(22+)$ to $Nb_6(26+)$ in aqueous bicarbonate should be represented by the equation

$$Nb_6(22+) + 4H_2O \longrightarrow Nb_6(26+) + 2H_2 + 4OH^-$$

and this explains the liberation of 0.67 g atoms of hydrogen per mole of Nb(3.67), itself, being converted to Nb(4.33).

Acknowledgements

We thank Dr (Mrs.) S. Sen of this Department and Swami Muktirupananda, Principal, Ramakrishna Mission Residential College, Narendrapur, for encouragement.

References

1 W. M. Nelson and R. S. Tobias, *Inorg. Chem.*, *2*, 985 (1963).
2 M. Filowitz, R. K. C. Ho, W. G. Klemperer and W. Shum, *Inorg. Chem.*, *18*, 93 (1979).
3 B. K. Sen, A. V. Saha and N. Chatterjee, *Mater. Res. Bull.*, *16*, 923 (1981).

4 B. K. Sen and A. V. Saha, *Mater. Res. Bull.*, *17*, 161 (1982).

5 B. K. Sen, P. Bandyopadhyay and A. V. Saha, *Mater. Res. Bull.*, *17*, 611 (1982).

6 B. K. Sen, P. Bandyopadhyay, Subha Sen and A. V. Saha, *Mater. Res. Bull.*, *18*, 19 (1983).

7 Y. Hosokawa, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, *48*, 3175 (1975).

8 I. Kiehl, R. Fox and H. Hardt, *J. Am. Chem. Soc.*, *59*, 2395 (1937).

9 E. W. Golibersuch and R. C. Young, *J. Am. Chem. Soc.*, *71*, 2402 (1949).

10 E. I. Krylov and N. N. Kalugina, *Zh. Neorg. Khim.*, *4*, 2476 (1959).

11 Ya G. Goroshchenko and M. I. Andreeva, *Russ. J. Inorg. Chem.*, *11*, 1197 (1966).

12 J. E. Finholt, R. W. Anderson, J. A. Fyfe and K. G. Caulton, *Inorg. Chem.*, *4*, 43 (1965).

13 C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).

14 R. Eskenazi, J. Raskovan and R. Levitus, *J. Inorg. Nucl. Chem.*, *28*, 521 (1966).

15 C. S. Alleyne, K. O. Mailer and R. C. Thompson, *Can. J. Chem.*, *52*, 336 (1974).