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Complexation of Niobium(V) with Some Bis-(β-diketones)

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The complexes of niobium(V) with 2-phenyl-1,1,3,3-tetraacetylpropane and 2-phenyl-1,3-diacetyl-1,3-dibenzoylpropane were investigated by IR, UV, ^{1}H-NMR, and magnetic measurements. Together with analytical data and determination of molecular weights a trimeric structure is proposed for both 1 : 1 complexes.

[Keywords: Niobium(V) complexes; ^{1}H-*NMR; Magnetic measurements]*

Komplexierung von Niob(V) mit einigen Bis(β-diketonen)

Es wurden die Komplexe von Niob(V) mit 2-Phenyl-1,1,3,3-tetraacetylpropan und 2-Phenyl-1,3-diacetyl-1,3-dibenzoylpropan untersucht. IR-, UV- und ^{1}H-NMR-Spektren sowie magnetische Messungen zusammen mit analytischen Daten und Molekulargewichtsbestimmungen ergaben für beide 1 : 1 Komplexe eine trimere Struktur.

Use of coordination compounds of β-diketones in laser technology, NMR shift reagents, gas chromatography, solvent extraction, spectral studies etc., is well known. Bis-(β-diketones) which are synthesised from β-diketones are double-faced bidentate ligands. Owing to the high coordination tendency due to the presence of an oxygen atom in the keto-enol form the bis-(β-diketones) have a tendency to form six-membered ring with metal ions.

A large number of bis-(β-diketones) are reported in literature[1] but their complexation with niobium has not been studied so far. In view of the increasing applications of niobium in reactor technology, electronics, areospace materials and its bio-activity, it was considered worthwhile to investigate the complexation of Nb(V) with some bis-(β-diketones). In the present paper synthetic and spectrophotometric studies on the complexation of niobium(V) with 2-phenyl-1,1,3,3-tetraacetylpropane [*PTAP*] and 2-phenyl-1,3-diacetyl-1,3-dibenzoylpropane [*PDADBP*] are presented.

Experimental

Preparation of 2-Phenyl-1,1,3,3-tetraacetylpropane (PTAP) and 2-Phenyl-1,3-diacetyl-1,3-dibenzoylpropane (PDADBP)

These compounds were prepared by the method described by *Fernelius* and coworkers[1]. They are white compounds and have melting point 161 °C and 198 °C respectively. The compounds were characterized by elemental analysis, IR, electronic and NMR spectra.

Niobium-Pentachloride Solution

A known weight of niobium-pentachloride (Fluka) was dissolved in dry methanol. Care was taken to avoid moisture while weighing and preparing the solution. This stock solution was diluted to required concentrations with dry methanol.

Preparation of (a) Niobium-2-phenyl-1,1,3,3-tetraacetylpropane and (b) Niobium-2-phenyl-1,3-diacetyl-1,3-dibenzoylpropane Complexes

(a) On mixing the solution of $NbCl_5$ and *PTAP* in dry methanol, a greenish solution was obtained. Further studies on this colour reaction were carried out spectrophotometrically.

$NbCl_5$ and the *PTAP* solution in methanol (1 : 1 mole ratio) were refluxed for about 17 h. On evaporating methanol under low pressure, a reddish-brown compound was obtained which was washed with benzene. It did not show a sharp melting point but decomposed between 227 °C to 230 °C.

(b) $NbCl_5$ and *PDADBP* solutions in dry methanol on mixing in 1 : 1 mole ratio gave a light green coloured solution. The colour was not found to be stable and mixture was refluxed for about 6 h. On concentrating the solution and placing it under low temperature, an orange compound separated which was dried under low pressure and then recrystallised from benzene. This compound too did not show any sharp melting point and decomposed above 223 °C.

Spectrophotometric Studies on Soluble Nb-*(PTAP) Complex*

Absorbance measurements were recorded on a Beckman DB spectrophotometer using optically matched 10 mm path length quartz cells. A $1.0 \cdot 10^{-2} M$ solution of the reagent in methanol was prepared. This solution was diluted to required concentrations during operation. A greenish colour developed on mixing equimolar solutions of the reagent and niobium(V); it became stable after 10 h. The complex solution exhibited maximum absorbance at 432 nm and the system obeyed *Beer*'s law up to the concentration 325 ppm.

Vosburgh and *Cooper*'s method[2] indicated the formation of only one complex under the experimental conditions. The modified *Job*'s equimolar and nonequimolar methods of continuous variation as modified by *Dey* et al.[3-5] and the *Yoe-Jones* mole ratio method[6] indicated a Nb: *PTAP* ratio of 1 : 1 in the complex.

The average value of the stability constant *K* for the Nb-*PTAP* complex was found to be $1.3966 \cdot 10^5$. The free energy of formation, ΔF°, calculated by *Vant Hoff*'s isotherm ($\Delta F^\circ = RT \ln K$) was found to be $-6897 - 3034$ K cal/mol at 300 K.

Elemental Analysis of the Solid Complexes of Nb(V) *with PTAP and PDADBP*

The constituents of the complex were determined by standard methods. The molecular weights were determined by the *Rast* camphor method and found to be 1 370 for the Nb-*PTAP* complex and 1 718 for the Nb-*PDADBP* complex.

		% C	% H	% Cl	% Nb
$NbC_{17}H_{18}O_5Cl$ (Nb-*PTAP* complex)	Calc.	47.39	4.18	8.25	21.60
	Found	47.34	4.27	8.31	21.63
$NbC_{27}H_{22}O_5Cl$ (Nb-*PDADBP* complex)	Calc.	58.43	3.97	6.40	16.77
	Found	58.37	4.01	6.42	16.81

IR Spectra

IR spectra of the complexes were recorded on a Perkin-Elmer Spectrophotometer Model 377 using KBr pellets. The assignments are given in Table 1.

Table 1. *IR-data* (cm^{-1})

PTAP	Nb-*PTAP* complex	*PDADBP*	Nb-*PDADBP* complex	Assignment
–	583	–	585	Nb–O
–	975 sho	–	937 sho	Nb=O
–	–	–	1 010 to 1 045 band	Ph–C and C=O
–	–	–	1 060 to 1 120 band	Ph–C and C=O
–	1 140 to 1 210 band	–	–	Ph–C and C=O
1 150 s	–	1 145 s	–	Ph–C, C–OH, and C=O
1 175 s	–	1 165 s	–	–do–
1 210 s	–	1 180 s	–	–do–
–	–	1 195 s	–	–do–
1 325 to 1 380 band	–	1 350 s	–	CH_3–C, C–OH, and CH
–	–	1 385 s	–	–do–
–	1 350 sho	–	1 385 to 1 450 band	CH_3–C and CH
–	1 500 to 1 640 band	–	1 500 to 1 540 band	C=O
1 690 s	–	1 675 s	–	C=O
1 710 s	–	1 700 s	–	C=O
3 425 s	–	3 350	–	C=OH

Electronic Spectra

Electronic spectra were recorded in ethanol on a Pye-Unicam automatic spectrophotometer using optically matched 10 mm quartz cells.

The absorption band of *PTAP* appears at 292 nm and that of the Nb-*PTAP* complex at 272 nm and 344 nm. The absorption band of *PDADBP* appears at 272 nm and that of the Nb-*PDADBP* complex at 272 nm and 372 nm.

^{1}H-*NMR Spectra*

^{1}H NMR spectra were recorded on a Varian XL-100 A NMR spectrometer using *DMSO*-d_6 as solvent and *TMS* as an internal standard (Table 2).

Table 2. ^{1}H-*NMR spectral data* (δ, *ppm*)

PTAP	Nb-*PTAP*	*PDADBP*	Nb-*PDADBP*	Assignment
1.2 s	2.56 s	1.42 s	2.56 s	CH_3
1.96 s	–	–	–	CH_3
4.06 m	4.38 s	4.1 m	4.2 s	CH near to phenyl
5.2	–	5.52	–	CH due to tautomerism
6.8 to 7.44 m	6.6 to 7.6 m	6.8 to 8.0 m	7.0 to 7.56	*Ph*-ring
–	8.4 to 9.1 m	–	8.48 to 9.3	*Ph*-ring

Magnetic Measurements

The magnetic susceptibility of the complexes was determined by a *Gouy* balance using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. The measurements were corrected only for diamagnetic corrections but not for temperature-independent paramagnetism. Both complexes appeared to be diamagnetic having μ_{eff} 0.4 BM and 0.32 BM respectively at 295 K.

Results and Discussion

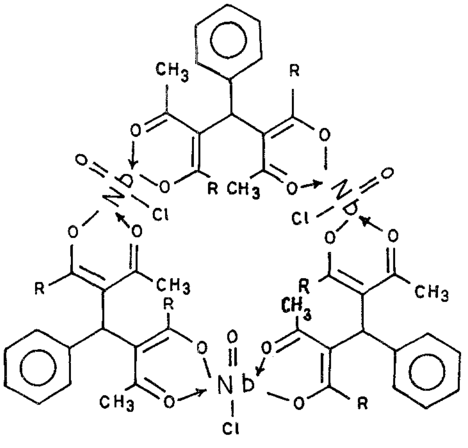
The presence of a OH band due to keto-enol tautomerism in *PTAP* and *PDADBP* spectra at 3 425 and 3 350 cm^{-1} is not observed for the complex spectra. The wide band in *PTAP* spectra at 1 350 to 1 380 cm^{-1} due to C–OH, →CH and C–CH_3 is converted into a small shoulder at 1 350 cm^{-1}. Similarly, for *PDADBP* the sharp peak at 1 385 and a shoulder at 1 350 cm^{-1} are converted into a small band at 1 385 to 1 450 cm^{-1} indicating that coordination takes place through the –OH bond.

The sharp peaks in the *PTAP* spectra at 1 710 and 1 690 cm^{-1} are shifted to lower range by nearly 60 cm^{-1} in the form of a wide band at 1 500 to 1 640 cm^{-1}. In the case of the Nb-*PDADBP* complex sharp peaks at 1 675 and 1 700 cm^{-1} are converted into a band at 1 500 to 1 540 cm^{-1}. These shifts suggest complex formation through the carbonyl group[7]. The lowering of ν (C = O) is much larger in the case of an aromatic ketone[7] as compared to an aliphatic ketone, which agrees with the fact that aromatic ketones have more polarisable carbonyl groups as compared to aliphatic ketones[8].

Sharp peaks in the *PTAP* spectra at 1 210, 1 150 and a shoulder at 1 175 cm^{-1} which may be due to C – OH, C = O and C – *Ph* are converted into a wide band at 1 210 to 1 140 cm^{-1} in the complex due to the presence of a monosubstituted phenyl ring and a carbonyl group. Similarly, the sharp peaks at 1 195, 1 180, 1 145 and a shoulder at 1 165 cm^{-1} in the *PDADBP* spectra are converted into a wide band at 1 120 to 1 060 and 1 010 to 1 045 cm^{-1} in the complex spectra. The ν (Nb – O) observed in the complex spectra at 583 and 585 cm^{-1} is also identical with the earlier reported frequency[9].

The ν (Nb = O) observed in the spectra of Nb-*PTAP* at 975 cm^{-1} and in Nb-*PDADBP* at 937 cm^{-1} is similar to the earlier reported frequencies in this region for such bonds[10–13].

The electronic spectra of the complexes shows no low energy band attributable to a d-d transition which is consistant with the d$^{\circ}$ electronic configuration[14] of the metal ion. The absorption band in *PTAP* at 292 nm may be due to $\pi \rightarrow \pi^*$ and $n - \pi^*$. In the Nb-*PTAP* complex two bands appear. The band at 272 nm may be due to a $\pi \rightarrow \pi^*$ and $n - \pi^*$ transition and the other at 344 nm may be due to charge transfer transitions. Similarly, in the case of *PDADBP* there is a band at 272 nm and in the Nb-*PDADBP* complex two bands appear at 272 nm and 372 nm.



Where R = CH$_3$ or C$_6$H$_5$

Integration of peaks in the PMR spectra could not be carried out because peaks due to the methyl protons in both the complexes are obscured by *DMSO*.

Methyl protons in the ligand *PTAP* appear as singlet at δ 1.2 and 1.96 and are shifted to 2.56 in the complex Nb-*PTAP*. In the case of the ligand *PDADBP*, the singlet at 1.42 is shifted to 2.56 in the Nb-*PDADBP* complex. The peaks due to the phenyl protons of the Nb-*PTAP* and Nb-*PDADBP* complexes appear up to 9.1 and 9.3 respectively. This considerable down-field shift in the peaks of the methyl and phenyl protons suggests that charge transfer of electrons takes place. Due to the net effect of high electronegative elements (O and Cl) attached to the niobium ion, the chelate ring possesses a positive charge. The down-field shift also suggests that the diketone molecule should be in plane with the niobium ion.

The doublet at 5.52 and peak at 5.2 in the respective spectra of the ligands *PDADBP* and *PTAP* due to the proton involved in keto-enol tautomerism are absent in the spectra of the complexes. The multiplet at 4.06 and 4.1 in the respective spectra of the ligands *PTAP* and *PDADBP* due to the → CH-proton in the viscinity of phenyl ring is converted into a singlet at 4.38 and 4.2, respectively in the case of the complexes. This supports the assumption that coordination takes place through the $-$OH bond.

In both complexes niobium ion appears to be diamagnetic. The small value of μ_{eff} may be due to temperature-independent paramagnetism.

On the basis of above studies and the molecular weight the following trimeric structure is preposed for the solid complexes. Spectrophotometric studies suggest a 1 : 1 (Nb: ligand) ratio for the Nb-*PTAP* complex formed in solution.

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References

[1] *Martin D. F., Shamma M., Fernelius W. C.*, J. Amer. Chem. Soc. **80**, 5851 (1958).
[2] *Vosburgh W. C., Cooper G. R.*, J. Amer. Chem. Soc. **63**, 437 (1941).
[3] *Job P.*, Ann. Chim. **9**, 113 (1928); **6**, 97 (1936).
[4] *Foley R. T., Anderson R. C.*, J. Amer. Chem. Soc. **71**, 909 (1947).
[5] *Mukherji A. K., Dey A. K.*, J. Inorg. Nucl. Chem. **6**, 314 (1958).
[6] *Yoe J. H., Jones A. L.*, Ind. Eng. Chem. Anal. Ed. **16**, 111 (1944).
[7] *Gill M. S., Ahuja H. S., Rao G. S.*, J. Less-Common Metals **21**, 447 (1970).

[8] *Cook D.,* Can. J. Chem. **39**, 1184 (1961).
[9] *Barradough C. G., Bradly D. C., Lewis J., Thomas I. M.,* J. Chem. Soc. (A) **1961**, 2601.
[10] *Brown D., Easey J. F., Du Preez J. G. H.,* J. Chem. Soc. (A) **1966**, 258.
[11] *Dordjevic C., Kotovic V.,* J. Inorg. Nucl. Chem. **25**, 1099 (1963).
[12] *Dordjevic C., Kalovic V.,* J. Chem. Soc. (A) **1970**, 3382.
[13] *Clark R. J. H., Kepert D. L., Nyholm R. S.,* J. Chem. Soc. **1965**, 2877.
[14] *Wilkins J. D.,* J. Inorg. Nucl. Chem. **37**, 2095 (1975).