

MONOTHIO- β -DIKETONE DERIVATIVES OF TITANIUM AND ALUMINIUM

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ABSTRACT

The preparation and physical properties of octahedral bis(monothio- β diketonato) dialkoxotitanium(IV), $\text{Ti}(\text{OR})_2(\text{R}'\text{CSCHCOR}'')$, aluminium isopropoxide derivatives, $\text{Al}(\text{OPr}^i)_2(\text{R}'\text{CSCHCOR}'')$ and $\text{Al}(\text{OPr}^i)(\text{MeCSCHCOMe})_2$ and aluminium tris(monothioacetylacetonate), $\text{Al}(\text{MeCSCHCOMe})_3$ are described. The complexes are monomeric in benzene (cryometrically) except $\text{Al}(\text{OPr}^i)_2(\text{R}'\text{CSCHCOR}'')$ which is found to be dimeric. Information about their stereochemistry has been deduced from IR and ^1H NMR data.

INTRODUCTION

THE chemistry of main group and early transition metal ions when complexed to monothio- β -diketones is not very clear¹⁻³. A number of later transition metals are known to combine with this ligand¹⁻³. From these it has been shown that the monothio- β -diketonates are different from their oxygen analogues as incorporation of sulphur changes the behaviour of the ketone remarkably. These and the stereochemical rigidity exhibited in octahedral complexes such as niobium and tantalum tetraalkoxo monothio- β -diketonates⁴ at ambient temperature stimulated us to synthesize and examine octahedral titanium(IV) monothio- β -diketonates and a few aluminium monothio- β -diketonates. These are described in this paper.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture throughout from chemicals and apparatus and also during the spectral measurements. All the solvents were purified (dried and distilled) by the standard methods. Monothio- β -diketones, $\text{R}'\text{CSCH}_2\text{COR}''$ ($\text{R}' = \text{R}'' = \text{Ph}$, Me ; $\text{R}' = \text{Ph}$, $\text{R}'' = \text{Me}$) were synthesized by the literature procedure⁵⁻⁸. Titanium isopropoxide, $\text{Ti}(\text{OPr}^i)_4$ (50°/0.1 mm) was prepared by the ammonia method⁹⁻¹¹ and tert-butoxide, $\text{Ti}(\text{OBu}^t)_4$ (81°/2 mm) by the transesterification reaction¹². Aluminium isopropoxide, $\text{Al}(\text{OPr}^i)_3$ (106°/1.5 mm) was prepared by the direct interaction of aluminium metal with isopropanol.

The m.p. of the compounds was determined in sealed capillary tubes. Elemental analyses (titanium, aluminium and sulphur) were carried out as already reported¹³⁻¹⁵. IR spectra of neat liquids or as nujol mulls were recorded using CsI plates (Perkin Elmer 621) in the range 4000–200 cm^{-1} . ^1H NMR spectra were recorded on a A-60 Varian spectrometer using TMS as an internal standard. Molecular weights were determined cryoscopically in benzene.

(a) General method for the preparation of titanium(IV) dialkoxo bis(monothio- β -diketonates), $\text{Ti}(\text{OR})_2(\text{R}'\text{CSCHCOR}'')$ (I)

Appropriate titanium (IV) alkoxide the monothio- β -diketone were mixed in benzene (~ 50 ml) in 1:2 molar ratio and the mixture refluxed for 1/2 hr in oxygen-free nitrogen atmosphere. Volatile materials were removed *in vacuo* and the yellow to orange products were obtained after finally drying at 35°/0.5 mm/2 hr. The solid products were crystallized by benzene/hexane or by benzene/light petroleum. The details of the reactions are tabulated in table 1.

(b) General methods for the preparation of aluminium alkoxo monothio- β -diketonates and aluminium tris(monothioacetylacetonate) (II)

Aluminium isopropoxide and corresponding monothio- β -diketones mixed in dry benzene (in 1:1 and 1:2 molar ratios) were kept overnight at room temperature ($\sim 38^\circ$). Aluminium tris(monothioacetylacetonate) was synthesized by heating aluminium isopropoxide and monothioacetylacetone in 1:3 molar ratio in benzene under dry N_2 atmosphere. Volatile materials were removed at reduced pressure to obtain crystalline solid products. The details of the reactions are summarized in table 1.

RESULTS AND DISCUSSION

Bis(monothio- β -diketonato) dialkoxotitanium(IV), $\text{Ti}(\text{OR})_2(\text{R}'\text{CSCHCOR}'')$ have been obtained by heating titanium tetraalkoxides and monothio- β -diketones in 1:2 molar ratio in refluxing benzene in an inert atmosphere:



($\text{R} = i\text{-Pr}$ and $t\text{-Bu}$; $\text{R}' = \text{R}'' = \text{Me}$, Ph ; $\text{R}' = \text{Ph}$, $\text{R}'' = \text{Me}$)

TABLE 1
Reactions of metal alkoxides with monothio- β -diketones

Reactants (g)				Molar ratio	Reaction condition (h)	Yield (%)	M.P. (°)	% Analysis found		Mol. wt. Found
M(OR) _n	R'CSCH ₂ COR''	R' =	R'' =					(Calcd.) M	S	(Calcd.)
1. Ti(OPr ⁱ) ₄	Me	0.76	Me	1:2	A (1/2)	65	—	12.8 (12.0)	16.9 (16.1)	355 (396)
2. Ti(OBu ^t) ₄	Me	0.70	Me	1:2	A (1/2)	90	d	11.0 (11.2)	14.7 (15.1)	452 (424)
3. Ti(OPr ⁱ) ₄	Ph	0.51	Me	1:2	A (1/2)	55	132	9.8 (9.2)	13.0 (12.3)	C
4. Ti(OBu ^t) ₄	Ph	0.40	Me	1:2	A (1/2)	62	142	8.9 (8.7)	12.0 (11.7)	C
5. Ti(OPr ⁱ) ₄	Ph	0.72	Ph	1:2	A (1/2)	68	162	7.8 (7.4)	10.2 (9.9)	678 (644)
6. Ti(OBu ^t) ₄	Ph	0.77	Ph	1:2	A (1/2)	65	175	7.8 (7.1)	10.1 (9.5)	695 (672)
7. Al(OPr ⁱ) ₃	Me	0.79	Me	1:1	B (8)	95	168	9.7 (10.3)	11.8 (12.3)	528 (260)
8. Al(OPr ⁱ) ₃	Ph	0.39	Ph	1:1	B (12)	90	148	7.0 (7.0)	8.4 (8.3)	D
9. Al(OPr ⁱ) ₃	Me	0.45	Me	1:2	B (12)	86	108	8.2 (8.5)	19.8 (20.2)	D
10. Al(OPr ⁱ) ₃	Me	0.32	Me	1:3	A (6)	84	130	6.9 (7.8)	27.2 (27.8)	D

A Heated under reflux; B Kept at room temperature ($\sim 30^\circ\text{C}$);

C By analogy these can be considered to be monomeric

D The data could not be obtained due to the poor solubility. The products of the reaction 9 and 10 are presumed to be monomeric on the basis of the analogous acetylacetonate derivatives^E

E Majis, L., Vevere, I., Brester, L. S., Tsereteli, I. Y., and Karabanova, E. I., Latv. P. S. R. Zinat, Akad. Vestis. Khim. Seri. 1971, 439; Chem. Abst., 1971, 75, 156828b.

The corresponding reactions with aluminium isopropoxide were facile and mono(monothioacetylacetonato)diisopropoxo aluminium and bis(monothioacetylacetonato) aluminium isopropoxide could be prepared even at room temperature. The reactants had to be heated to get tris(monothioacetylacetonato)aluminium.



+ PrⁱOH (N = 1-3)

The products are yellow-to-orange coloured crystalline sharp melting solids except Ti(OBu^t)₂(MeCSCHCOMe)₂ which is a yellow liquid and are monomeric in benzene (cryometrically). Mono(monothioacetylacetonato)diisopropoxo aluminium alone has been found to be dimeric under similar conditions.

Infrared spectral data of these titanium and aluminium derivatives have been helpful in understanding the mode of bonding of the ligand. The drop in the frequencies of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ observed respectively at 1652–1590 and 1571–30 cm^{-1} in the ligand^{2,3,16} to 1560–20 and 1475–25 cm^{-1} in the complexes is commensurate with the bidentate behaviour of the ligand^{2,3,16}. The symmetrical gem-dimethyl vibrations of isopropoxo derivatives are observed at ~ 1365 and ~ 132 cm^{-1} . In di-tert-butoxo titanium compounds absorption due to $\nu(\text{C}-\text{O})$ of the alkoxo group is observed at ~ 1005 cm^{-1} . The corresponding absorptions in the diisopropoxo products are noted at ~ 1115 and 985 ± 10 cm^{-1} . In isopropoxo aluminium derivatives, apart from two characteristic $\nu(\text{C}-\text{O})$ bands noted at 1165 and 1026 cm^{-1} for terminal isopropoxo groups, two additional absorptions at 1125 and 940 cm^{-1} are observed only in dimeric mono(monothio- β -diketonato)diisopropoxo aluminium assignable to the bridging isopropoxo group.

A medium intensity band in the region 680–50 cm^{-1} can be ascribed to $\nu(\text{Ti}-\text{O}) + \delta(\text{C}-\text{Me})$ or δ ring

vibrations¹⁷. $\nu(\text{Ti}-\text{O})$ modes have been found to occur at ~ 620 , 585 ± 10 and around 495–435 cm^{-1} ^{18–20}. The band at 696 ± 5 cm^{-1} in the aluminium derivatives may arise owing to $\nu(\text{Al}-\text{O})$ ²¹. The bands at ~ 390 and 360 cm^{-1} are assignable to $\nu(\text{Ti}-\text{S})$ vibrations in the titanium compounds^{20,22}.

^1H NMR spectral data (table 2) have thrown some light regarding the stereochemistry of these monothio- β -diketonates. Bis(monothioacetylacetonato) diisopropoxotitanium, $\text{Ti}(\text{OPr}^i)_2(\text{MeCSCHCOMe})_2$ at probe temperature ($\sim 44.5^\circ$) exhibits a doublet owing to gem- Me_2 (of the isopropoxo group), a singlet each for Me-CS, Me-Co and $-\text{CH} =$ protons. These data while concurrent with the *trans*-octahedral structure can also be interpreted due to *cis*-configuration undergoing fast exchange at NMR time scale like the earlier observation on the acetylacetonato analogue, $\text{Ti}(\text{OPr}^i)_2(\text{MeCOCHCOMe})_2$ ^{17,23–27}. The introduction of bulkier tert-butoxo group e.g. in $\text{Ti}(\text{OBu}^t)_2(\text{MeCSCHCOMe})_2$ bring about no change in the pattern of its ^1H NMR spectrum.

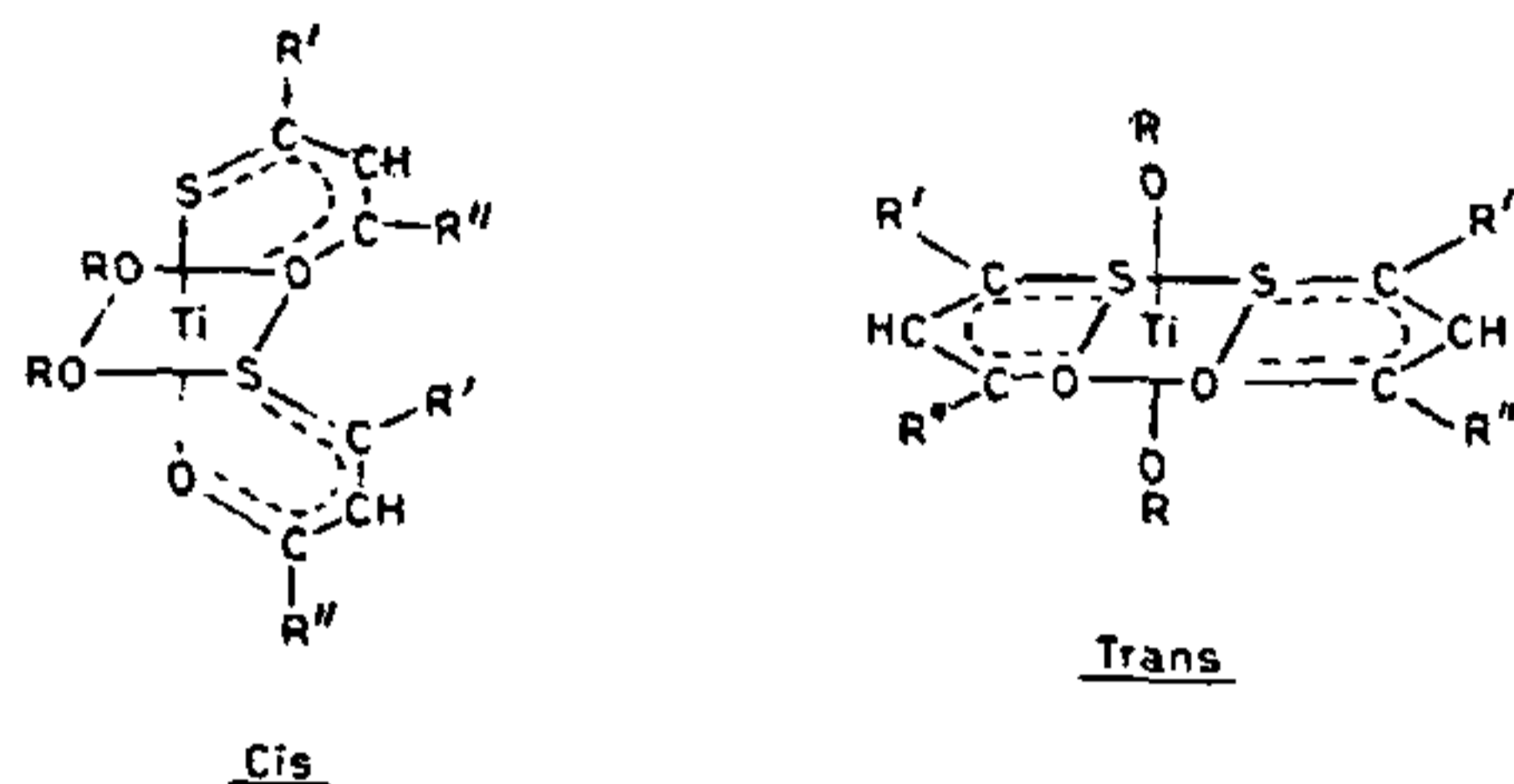
TABLE 2

^1H NMR Spectral data of titanium and aluminum monothio- β -diketonates

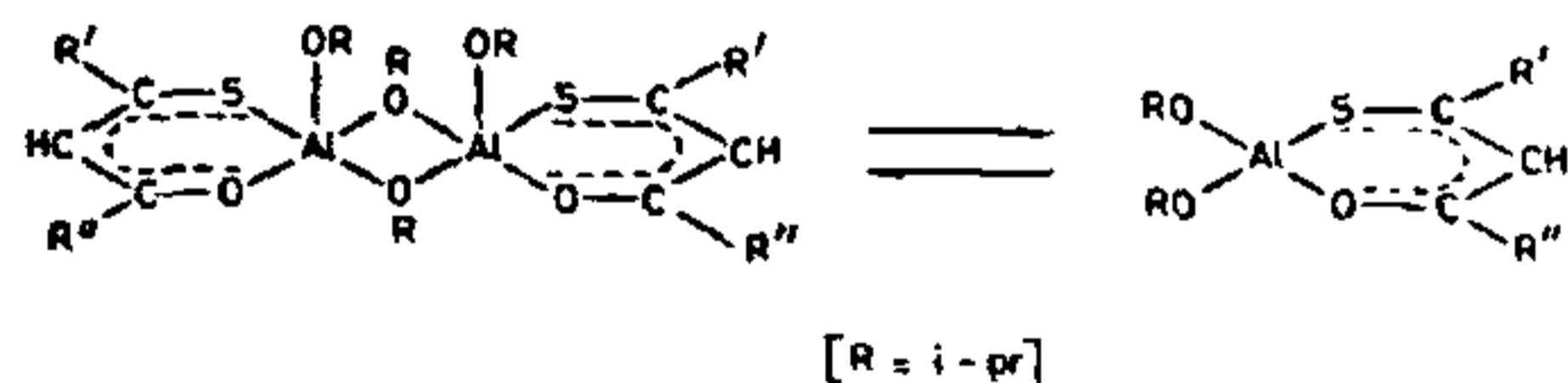
S. No.	Compounds	Proton signals (δ)			
		Me-CS (3H)	Me-Co (3H)	PhCS(5H) and/ or PhCO (5H)	= CH- (1H) Protons of alkoxo group
1.	$\text{Ti}(\text{OPr}^i)_2(\text{MeCSCHCOMe})_2$	2.38	2.10	—	6.40 —CH < 4.91s; gem- Me_2 1.21d
2.	$\text{Ti}(\text{OBu}^t)_2(\text{MeCSCHCOMe})_2$	2.36	2.08	—	6.40 $\text{Me}_3\text{C}-$, 1.30
3.	$\text{Ti}(\text{OPr}^i)_2(\text{PhCSCHCOMe})_2$	—	2.23	7.25–7.90	6.81, 6.75 —CH < , 5.01s; gem- Me_2 1.28d 1.15d
4.	$\text{Ti}(\text{OBu}^t)_2(\text{PhCSCHCOMe})_2$	—	2.23	7.25–7.90	6.76, 6.68 $\text{Me}_3\text{C}-$, 1.36, 1.21.
5.	$\text{Ti}(\text{OPr}^i)_2(\text{PhCSCHCOPh})_2$	—	—	7.25–8.23	A —CH < , 5.10s; gem- Me_2 1.35d, 1.16d
6.	$\text{Ti}(\text{OBu}^t)_2(\text{PhCSCHCOPh})_2$	—	—	7.25–8.23	A $\text{Me}_3\text{C}-$, 1.41, 1.23
7.	$\text{Al}(\text{OPr}^i)_2(\text{MeCSCHCOMe})_2$	2.36	2.15	—	6.40 —CH < 4.40s; gem- Me_2 , 1.50d, 1.30d, 1.13d
8.	$\text{Al}(\text{OPr}^i)_2(\text{PhCSCHCOPh})_2$	—	—	7.20–8.30	A —CH < 4.45s; gem- Me_2 , 1.48d, 1.30d, 1.11d
9.	$\text{Al}(\text{OPr}^i)_2(\text{MeCSCHCOMe})_2$	2.35, 2.28	2.05, 1.96	—	6.21 —CH < 4.40s; gem- Me_2 , 1.03d
10.	$\text{Al}(\text{MeCSCHCOMe})_3$	2.43	2.21	—	6.55 —

Solvent CCl_4 , TMS was used as an internal standard. A = Mixed with phenyl singlets, d = doublet, s = septet.

Interestingly, in $\text{Ti}(\text{OR})_2(\text{PhCSCHCOMe})_2$ and $\text{Ti}(\text{OR})_2(\text{PhCSCHCOPh})_2$ with phenyl groups at 2,4 positions in the thio- β -diketonate moiety, the pattern of ^1H NMR spectra is different. In these at the probe temperature two sets of signals due to alkoxo protons have been obtained in unequal intensities. Furthermore, the ring proton in $\text{Ti}(\text{OR})_2(\text{PhCSCHCOMe})_2$ has also been found to split into two peaks of unequal but of comparable intensities with that of the alkoxo signals. These findings can be assumed to be due to a mixture of *cis*- and *trans*-octahedral forms²⁸ (figure 1). It may, however, be mentioned that in- β -diketonates, the increased steric factor in the alkoxo as well as in the β -diketonate moiety does not bring about any change in the stereochemistry and the complex $\text{Ti}(\text{OC}(\text{Me})_2\text{Ph})_2(\text{Bu}'\text{COCHCOBu}')_2$ remains *cis*²⁵.



The ^1H NMR spectra of mono(monothio- β -diketonato) aluminium diisopropoxide exhibit three doublets for gem- Me_2 protons of isopropoxo groups in 1:1:2 ratio. This can probably be understood in terms of an equilibrium of monomeric and dimeric species at the probe temperature (figure 2).



In the spectrum of bis(monothioacetylacetonato) aluminium isopropoxide, a doublet for gem- CH_3 and two sets of signals of monothioacetylacetonato protons suggest trigonal bipyramidal geometry. Octahedral tris(acetylacetonato)aluminium(III) exhibits single set of signals.

For the complexes investigated here, differentiation of the *cis*- and *trans*-isomers is tentative provided slow exchange can be reached and chemical shift differences between inequivalent sites is resolvable for which, variable NMR data are essential.

ACKNOWLEDGEMENT

The authors are thankful to CSIR, New Delhi for the award of post-doctoral fellowships (RKK and CKN).

- Livingstone, S. E., *Coord. Chem. Rev.*, 1971, 7, 59.
- Cox, M. and Darken, J., *Coord. Chem. Rev.*, 1971, 7, 29 and references therein.
- Mehrotra, R. C., Bohra, R. and Gaur, D. P., *Metal β -diketonates and allied derivatives*, Academic Press, 1978.
- Kanjolia, R. K. and Gupta, V. D., *Inorg. Nucl. Chem. Lett.*, 1980, 16, 449.
- Uhlemann, E. and Muller, H., *Angew. Chem. Intern. Ed. Eng.*, 1965, 4, 154.
- Uhlemann, E. and Thomas, P., *J. Prakt. Chem.*, 1966, 34, 180.
- Yokoyama, A., Kawanishi, S., Ouikuma, M. and Tanaka, H., *Chem. Pharm. Bull. (Tokyo)*, 1967, 15, 540.
- Duus, F. and Anthonson, J. W., *Acta Chem. Scand. B.*, 1977, 31, 40.
- Nells, J., *Br. Patent*, 1939, 512, 452.
- Nells, J., *US Patent*, 1940, 2, 187, 721.
- Cullinane, M. M., Chard, S. J., Price, C. F. and Milward, B. P., *J. Soc. Chem. Ind. London*, 1950, 69, 538, (*Chem. Abst.*, 1951, 45, 7950).
- Mehrotra, R. C., *J. Am. Chem. Soc.*, 1954, 76, 2266.
- Kanjolia, R. K., Ph.D. Thesis, B.H.U., Varanasi, India, 1981.
- Vogel, A. I., *A textbook of quantitative inorganic analysis*, (IV Edition), Longman Group Ltd., London, 1978.
- Saraswat, B. S., Srivastava, G. and Mehrotra, R. C., *J. Organometal Chem.*, 1977, 129, 155.
- Uhlemann, E., Miller, H. and Thomas, P., *Z. Chem.*, 1971, 11, 401.
- Bradley, D. C. and Holloway, C. E., *J. Chem. Soc. (A)*, 1969, 282.
- Barraclough, C. G., Bradley, D. C., Lewis, J. and Thomas, I. M., *J. Chem. Soc.*, 1961, 2601.
- Lynch, C. T., Mazdiyasni, K. S., Smith, J. S. and Crawford, W. J., *Anal. Chem.*, 1964, 36, 2332.
- Hawthorne, S. L. and Fay, R. C., *Am. Chem. Soc.*, 1979, 101, 5268.
- Mehrotra, A. and Mehrotra, R. C., *Inorg. Chem.*, 11, 2170.
- Bhushan, B., Mittal, I. P., Chatwal, G. R. and Kaushik, N. K., *J. Inorg. Nucl. Chem.*, 1979, 41, 159.
- Bradley, D. C. and Holloway, C. E., *Chem. Commun.*, 1965, 284.
- Finocchiaro, P., *J. Am. Chem. Soc.*, 1975, 97, 4443.
- Fay, R. C. and Lindmark, A. F., *J. Am. Chem. Soc.*, 1975, 97, 5928.
- Haworth, D. T. and Wilkie, C. A., *Inorg. Nucl. Chem. Lett.*, 1977, 13, 485.
- Wilkie, C. A., Lin, G. and Haworth, D. T., *J. Inorg. Nucl. Chem.*, 1978, 40, 1009.
- Fay, R. C. and Lowry, R. N., *Inorg. Chem.*, 1967, 6, 1512.