STUDIES ON COPPER(I) COMPLEXES OF SOME MONOARYL THIOUREAS

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The copper(I) complexes of o-tolyl-, phenyl-, o-anisyl- and o-chlorophenyl thiourea have been prepared. The IR, NMR and thermal analysis of these complexes has shown that the coordination occurs through the nitrogen atom of the NH_2 group except in the case of o-tolyl thiourea complex where it is through the substituted nitrogen atom. The complexes are either monomeric or dimeric in nature.

Metal complexes of thiourea and substituted thioureas are extensively studied by electronic and vibrational spectroscopy[1–6]. Thiourea and its substituted derivatives appear generally to coordinate to metals through the sulphur atom, although in some cases bonding through nitrogen has also been reported[1,5,7–9]. It appears that very little attention has been paid to nitrogen bonded thiourea in metal complexes and also limited work has been done on the NMR behaviour of the thiourea metal complexes[10,11]. In the present paper we have tried to correlate the NMR behaviour of the complex with the mode of attachment of metal to ligand, in order to support our observations from the IR spectra.

Thermal decomposition studies of metal complexes have shown various correlations of decomposition temperatures with the metal ion, ligand character or counter-ion[12–14]. But thermal studies for thiourea and substituted thiourea metal complexes are limited to a few thiourea complexes of nickel(II) (ref.[15]), molybdenum[16], and a few substituted thiourea complexes of Cr(III), Mn(II), Co(II), Ni(II) and Cd(II) (ref.[17]). Almost no work on the thermal decomposition behaviour of aryl thiourea metal complexes seems to have been done.

The present comunication deals with the studies of the Cu(I) complexes with various monoaryl thioureas, in order to ascertain the metal to ligand bond and their meric nature with the help of IR, NMR and thermal studies.

EXPERIMENTAL

Preparation of the Ligands

N-aryl substituted thioureas *i.e.*, *o*-tolylthiourea (ottu), phenylthiourea (ptu), *o*-anisylthiourea (oatu), and *o*-chlorophenylthiourea (ocptu) as ligands were prepared from corresponding aryl-amine hydrochlorides and ammonium thiocyanates by Kurzer's method[18]. Ammonium thio-cyanate was of Merck (G.R.) grade and was used as such. Copper(II) chloride and copper(II) sulphate were of AnalaR grade of B. D. H. (India). Arylamines were also of analytical grade.

Preparation of Copper(I) Complexes of Substituted Thioureas

For the preparation of Cu(I) complexes, Cu(II) salts were used, which were reduced to Cu(I) by substituted thioureas.

Preparation of N-arylthiourea-chlorocopper(I) complexes. To the ethanolic solution of the ligand the solution of copper(II) chloride in the same solvent was added slowly with constant stirring. The molar ratio of ligand to metal was kept 3 : 1. A white precipitate was obtained after stirring the solution for about half an hour. The precipitate was filtered under suction and washed several times with ethanol. Purification of the complex was done by dissolving it in chloroform and then reprecipitating with ethanol and finally it was dried in vacuum. All the complexes prepared were white crystalline solids, insoluble in water and ethanol, sparingly soluble in chloroform and dioxane, decomposed by N,N′-dimethylformamide.

Preparation of N-arylthiourea-sulphatocopper(I) complexes. To a warm aqueous solution of the ligand, cold aqueous solution of copper(II) sulphate was slowly added with constant stirring. The molar ratio of metal to ligand was 3 : 1. The mixture was continuously stirred for about half an hour and the coagulated precipitate was allowed to settle. The complex was then filtered and washed with water thoroughly and then dried in vacuum. All these complexes were pale yellow white solids, slightly soluble in dioxane and decompose in N,N′-dimethylformamide.

Characterization of Complexes

Analysis. For the determination of copper content a weighed amount of complex was repeatedly evaporated with small amounts of concentrated nitric acid till the residue gave a transparent clear solution with dilute hydrochloric acid. This solution was used for iodometric determination of copper. Sulphur in the complex was determinated as barium sulphate by Messenger's method. Chlorine was determinated by Stepnov's method. The results of the analyses are presented in Ta-ble I.

Conductivity and magnetic susceptibility measurements. The conductivity of the copper(I) complexes was measured on Phillips GM 4144 conductivity bridge. Gouy's method was employed to measure the magnetic susceptibility of the prepared complexes at room temperature using $CuCl_2 . 2 H_2O$ as standard.

Spectral studies. The IR spectra in KBr pellets were recorded on Perkin–Elmer Grating In-frared Spectrometer Model-577, in the range of $4000 - 6000 \text{ cm}^{-1}$. NMR spectra were recorded on Varian A 60D in deuterated chloroform using tetramethylsilane as internal standard.

Thermogravimetric studies. Thermogravimetric experiments were carried out using a thermo-balance assembled from Cahn RG Electrobalance, a Nichrome-wound furnace, temperature controller (Model 400), temperature programmer (Model 500) and a multipen recorder Rikadenki). Weight *vs* time, temperature *vs* time, d*w*/d*t vs* time plots were recorded on a three pen recorder.

The sample holder was a platinum boat and the thermocouple junction was placed within 1—2 mm directly under the sample holder. A 16 mm diameter silica hangdown tube isolated the dry argon sample environment flowing at a rate of 10 ml/min. Argon was dried by passing through molecular sieve 5A columns before entry into hangdown tube. The heating rate was 7°C/min and the complexes were heated in the temperature range 30 to 800°C.

RESULTS AND DISCUSSION

Nature of the Complexes Prepared

During the preparation of the complexes, the molar ratio of ligand to metal ion was kept 3 : 1, as this was found to be the optimum ratio to obtain the maximum yield of the complex under the given experimental conditions. If the metal ion was taken in excess of this ratio, copper(I) complex could not be precipitated and instead sticky oil like substance appeared on stirring, that after a prolonged stirring could only be separated out as yellowish, somewhat resinous, solid and proved not to be the desired complex (probably sulphur). On the other hand, when ligand was taken in excess, yield of the copper(I) complex was very poor and also its purification was difficult due to admixture of thiourea ligand.

The conductivity of the solution of the copper(I) complexes in chloroform ($c = 1·6 . 10^{-4}$ mol/l) was negligibly higher than that of the pure solvent and even for the saturated solutions of the complexes there was no visible difference. This is indicative of non-electrolytic behaviour of the complexes. The very low values of magnetic susceptibility indicate the diamagnetic nature of these complexes. Accor-

TABLE I

Analytical data % of the complexes prepared

Complex	Copper		Sulphur		Chlorine	
	calc.	found	calc.	found	calc.	found
[Cu(ptu)$_3$Cl]	11·45	11·60	17·30	17·25	6·40	6·35
[Cu(ottu)$_3$Cl]	10·64	10·82	16·08	16·00	5·94	5·90
[Cu(oatu)$_3$Cl]	9·85	9·89	14·88	14·75	5·50	5·43
[Cu(ocptu)$_3$Cl]	9·65	9·80	14·58	14·46	21·56	21·45
[{Cu(ptu)$_3$}$_2$SO$_4$]	11·20	11·28	19·73	19·67	—	—
[{Cu(ottu)$_3$}$_2$SO$_4$]	10·42	10·57	18·37	18·23	—	—
[{Cu(oatu)$_3$}$_2$SO$_4$]	9·66	9·69	17·03	16·93	—	—
[{Cu(ocptu)$_3$}$_2$SO$_4$]	9·47	9·62	16·69	16·51	—	—

ing to Palmer[19], substituted thioureas reduce Cu(II) salts used in the preparations of the complexes into Cu(I), being oxidized initially at normal temperature probably to disulphides which on heating further develop reducing power. Finally cyanamides and a deposit of sulphur are being produced. The white or yellowish white colours of the complexes are indicative of Cu(I) state which shows there is no influence of atmospheric oxygen in converting Cu(I) to Cu(II) state. Further, the diamagnetism of these complexes is also conclusive of absence of unpaired electrons confirming d[10] configuration of Cu(I) state in the complexes. Generally, copper in both the higher and lower valency states may be stabilized by appropriate bonding groups[20]. Ligands with σ bonding properties stabilize the bivalent state while with π bonding properties ligands such as acetonitrile[21], thiocarbamide[22], or ethylene thiocarbamide[23] give rise to the stabilization of Cu(I) state in copper complexes. The thiosulphato Cu(I) complex[24] in which the copper is coordinated to sulphur, like in the thiocarbamide compounds, also possesses considerable stability.

Infrared Spectra

The IR spectra of the ligands, the substituted thioureas and the corresponding copper-(I) complexes are compared in Table II. The IR spectra of the ligands are quite complex. Our assignments are based on a comparison of the bands of these molecules with IR bands of urea, thiourea, substituted thioureas and other structurally similar molecules. Only the peaks which help to infer the mode of attachment of these ligands to the metal ion are given in Table II.

The band present in the spectra of the ligands above 3 000 cm^{-1} can be attributed to the NH stretching vibrations. The corresponding bands observed for their Cu(I) complexes are shifted towards lower frequency and are somewhat broader. The lowering of ν(NH) frequency indicates bonding through nitrogen and broadening of the bands indicates considerable hydrogen bonding in the complexes.

The NH stretching bands in *o*-chlorophenylthiourea are broader and are shifted towards higher frequency on complexation, which may be due to the fact that in the ligand, thioamide hydrogen is intramolecularly hydrogen bonded to the chlorine, substituted in *ortho* position on the phenyl group. Similar type of hydrogen bonding has also been shown by Stewart and Siddall[25] in their studies with *ortho* substituted anilides. Probably there is less tendency to hydrogen bonding in the copper(I) complexes because of the increased steric hindrance and hence the NH stretching frequency increases.

In the complexes of *o*-tolylthiourea, the highest frequency ν(NH) band is shifted towards higher frequency side and is comparatively sharper than the lower NH stretching vibration frequency which is shifted towards lower frequency side and is broader. In the complexes with the other ligands, it is the lower frequency band which is more affected on complexation. This suggests that in the *ortho* copper(I) complexes the bonding mode is different than that in other complexes.
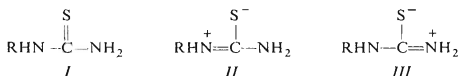
TABLE II

Selected IR spectral bands of the complexes and their free ligands (frequencies in cm^{-1}). Abbreviations: s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder

Compound	Assignment				
	ν(NH)	(NH$_2$)	N—C—S(I)	N—C—S(III)	ν(C—S)
ptu	3 420 s	1 610 s	1 520 s, br	1 050 s	750 s
	3 270 s				
	3 180 s				
[Cu(ptu)$_3$Cl]	3 400 br	1 605 s	1 525 s	1 085 sh	750 s
	3 250 br			1 070 s	
	3 170 br				
[{Cu(ptu)$_3$}$_2$SO$_4$]	3 360 br	1 595 s	1 515 m, s	1 090 vs^a	745 s
	3 260 br				
	3 180 br				
ottu	3 380 s	1 620 s	1 525 sh	1 040 s	760 s
	3 270 s				
	3 180 s				
[Cu(ottu)$_3$Cl]	3 420 s	1 605 s	1 520 ms, br	1 070 s	755 vs
	3 240 br				
	3 150 br				
[{Cu(ottu)$_3$}$_2$SO$_4$]	3 430 s	1 600 s	1 525 w	1 100 vs^a	760 s
	3 320 s				
	3 200 sh				
	3 170 s, br				
oatu	3 475 s	1 610 vs	1 535 vs	1 065 s	770 vs
	3 340 s				
	3 180 s				
[Cu(oatu)$_3$Cl]	3 400 br	1 605 vs	1 525 s	1 070 br	760 vs
	3 250 br				
	3 170 s				
[{Cu(oatu)$_3$}$_2$SO$_4$]	3 390 s	1 590 s	1 540 w	1 090 m^a	750 s
	3 240 br				
	3 160 br				
ocptu	3 340 s, br	1 605 vs	1 545 vs	1 055 ms	760 vs
	3 240 s, br				
	3 170 s, br				
[Cu(ocptu)$_3$Cl]	3 420 br	1 605 vs	1 520 s, br	1 075 w	755 vs
	3 340 w, br			1 055 s	
	3 250 m, br				
	3 160 s				
[{Cu(ocptu)$_3$}$_2$SO$_4$]	3 460 sh	1 600 s, br	1 555 ms (split)	1 090 vs^a	760 s
	3 350 s				
	3 260 m, br				
	3 150 br				

^{a} Band overlapped by strong absorption due to sulphate group.

Although the coordination of metal to sulphur is very common in thioureas metal complexes yet occassionaly coordination through nitrogen has also been observed. Coordination of Cu(I) to nitrogen atom has been observed in our studies which may by explained as follows. Kumler and Fohlen[26] have suggested resonance structures for thiourea with $20-30\%$ contribution of highly polar structures. Almost equal contribution of three canonical forms has been shown by IR, Raman and crystallographic studies[27]. In case of monoaryl thioureas also, three resonating structures may be represented as:

$$
\begin{array}{ccc}
\overset{\displaystyle S}{\underset{\displaystyle \|}{}} & \overset{\displaystyle S^-}{\underset{\displaystyle |}{}} & \overset{\displaystyle S^-}{\underset{\displaystyle |}{}} \\
RHN-C-NH_2 & RHN\overset{+}{=}C-NH_2 & RHN-C\overset{+}{=}NH_2 \\
I & II & III
\end{array}
$$

Thus the C–N bonds of the thioureas possess appreciable double bond character. Coordination through sulphur will make the unpaired electrons on the sulphur atom less available for bonding with thiourea unit. This means the cannonical forms *II* and *III* will assume increased importance over the form *I* with the result of decreased double bond character of C=S bond and increase in double bond character of C—N bond. Hence in sulphur bonded complexes the C—S frequencies should decrease and that of C—N bond should increase, while N—H frequency should remain unchanged. On the contrary, when metal–nitrogen bond is formed, just the opposite has to be expected with the reduction in N—H stretching.

In our work, the $\nu(N—H)$ frequencies observed in 3μ region are shifted towards lower frequency, which suggests the nitrogen coordination. If coordination of metal had been through sulphur atom these bands would not have been changed. Metal to ligand bonding through nitrogen atom is further supported by the shift of NH_2 deformation vibrations near $1\,600\,\text{cm}^{-1}$ towards lower frequency. Thioamide I band which involves a larger contribution from NH and C—N vibrations is either shifted towards lower frequency or its intensity is reduced on complexation. Thioamide *III* band involving mainly C=S stretching vibrations, appears near $1\,050\,\text{cm}^{-1}$ and is shifted towards higher frequency in copper(I) chloro complexes while it is obscured by the very strong absorption due to sulphate group near $1\,090\,\text{cm}^{-1}$. This indicates increased double bond character of the C—S bond (larger contribution of form *I*). The other bands are not much affected on complexation. The unaffected C—S stretching vibrations near $750\,\text{cm}^{-1}$ further support our inference. It is, therefore, evident from these observations that in all these complexes the coordination occurs through nitrogen atom. The similar type of nitrogen bonding has also been observed in the copper(I) complexes of *p*-tolylthiourea[28].

The bidentate coordination of sulphate group in copper(I) sulphate complexes is evident from the appearance of bands near $1\,090, 970, 610$ and $460\,\text{cm}^{-1}$. Nakamoto and coworkers[29] also observed the bands similar to ours and inferred the bidentate

nature of sulphate group. Three coordinating sites of Cu(I) are occupied by three nitrogen donor atoms, only one position in each complex remaining for coordination of the SO_4^{2-} group. Because this group, as follows from the vibrations observed, is bidentate, it means that it behaves as a bridge spanning two manomeric units in which copper(I) posesses the coordination number four while without bridge the coordination number of Cu(I) should be three.

NMR *Spectra*

The IR spectrum of $[Cu(ottu)_3Cl]$ indicated a somewhat different mode of bonding, hence its structure was further explored by comparing its NMR spectrum with that of the ligand. As the chemical shift value in NMR is also a function of solvent and temperature, the spectra were determined for both the ligand and the complex at the same temperature and in the same solvent, viz. deuterated chloroform. Hence the role of the solvent and temperature may not be very decisive for the observed chemical shifts. However, even if we believe that the solvent may interact differently with the ligand and the complex, then also owing to the low polarity of $CDCl_3$ interaction with the solvent (hydrogen bonding etc.) must be negligible. On the basis of the IR and analytical data, the structure of the complex may be assigned in two forms (Scheme 1). The NMR spectra of the ligand and of the complex were recorded in $CDCl_3$ at room temperature in order to find out changes in the chemical shifts due only to complexation. Comparative data of chemical shifts of the ligand and the complex have been shown in Table III. From this table it is inferred that: *a*) The signal due to methyl protons has been shifted to slightly lower σ values in the complex, indicating the deshielding of methyl protons which may be due to the complexation of substituted nitrogen atom with the metal ion. *b*) The proton on the substituted nitrogen atom also experiences deshielding as its NMR signal is shifted to lav field. *c*) The signal due to NH_2 protons is shifted somewhat upfield suggesting deshielding of these protons which shows that the coordination does not occur through the unsubstituted nitrogen atom. If the coordination had been through the NH_2 group, then the signal due to these protons would have shifted downfield.

TABLE III

The chemical shifts, δ (ppm), for protons of *o*-tolylthiourea and its copper(I) chloro complex

Group	ottu	$[Cu(ottu)_3Cl]$		Shift	
—CH_3	2·23	2·29	+0·06	downfield	deshielding
—NH	8·00	8·30	+0·30	downfield	deshielding
—NH_2	7·27	7·10	−0·17	upfield	shielding

These observations along with the shift of the NH stretching frequencies confirm the bonding between ligand and copper (I) through the substituted nitrogen and hence we propose that the structure (a) (Scheme I) for this complex is more appropriate. Although steric hindrance may be very effective in this structure (a), the basicity of the donor atom plays much more important role in complexation. The presence of benzene ring with an electron releasing substituent (methyl group) enhances the basicity of the substituted nitrogen atom and thus the structure (a) is the more probable one

Thermogravimetric Analysis

Thermogravimetric data in flowing argon atmosphere (Table IV) for the copper(I) sulphate complexes with all four ligands has been taken. The data indicates that the complexes decompose in gradual manner. These complexes have not been found to be thermally more stable in comparison with cobalt(II) and nickel(II) complexes with the similar ligands[30] which were also polymeric in nature.

The *o*-chlorophenylthiourea copper(I) complex, which is dimeric in nature, loses four ligand molecules at 210°C, another ligand molecule is lost at 240°C and

TABLE IV

Thermogravimetric data of substituted thiourea-copper(I) sulphato complexes, $[\{Cu(tu)_3\}_2SO_4]$

T °C	Percentage weight loss of complexes			
	ptu	ottu	oatu	ocptu
160	1·76	0·75	5·88	2·46
180	8·09	1·51	6·62	2·76
200	30·59	3·03	30·15	5·74
210	43·38	7·20	34·97	52·19
220	54·41	33·08	48·53	59·02
240	61·76	71·72	57·35	69·26
260	65·59	74·49	60·29	71·58
280	67·35	75·51	62·50	73·22
300	69·12	76·52	63·24	74·04
400	75·74	81·57	74·27	78·14
500	79·71	84·61	77·21	81·25
600	81·62	85·86	79·12	83·33
700	83·53	87·12	81·18	85·25
800	86·47	87·37	—	—

the last sixth organic molecule is gradually lost up to 600°C. With other complexes, initially two ligand molecules are lost and the remaining four ligand molecules break into small fragments and volatilize up to 700°C. If the decomposition temperature is taken as the measure of the thermal stability then the order of stability can be shown as

$$[\{Cu(ottu)_3\}_2SO_4] > [\{Cu(ocptu)_3\}_2SO_4] > [\{Cu(oatu)_3\}_2SO_4]$$
$$[\{Cu(ptu)_3\}_2SO_4]$$
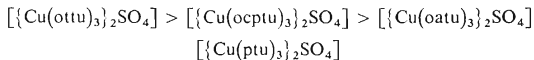
This is also the order of decreasing energy of activation at the decomposition temperature (Table V). But since the decomposition temperatures for these complexes are very close (210 ± 10°C, see Fig. 1), we employ the percentage weight loss at the de-

TABLE V

Activation parameters of the copper(I) sulphato complexes: T_i inflection temperature, *i.e.* DTG maximum temperature, w_i weight at T_i, $(dw/dt)_i$ rate of change in weight (heating rate 7°C/min), E energy of activation, Z frequency factor (E and Z calculated by Fuoss equation[31])

Complex	T_i K	w_i %	$(dw/dt)_i$	E	Z
				kJ/mol	
$[\{Cu(ptu)_3\}_2SO_4]$	473	30·59	1·125	67·98	$0·154 . 10^6$
$[\{Cu(ottu)_3\}_2SO_4]$	493	33·08	1·502	91·44	$0·280 . 10^8$
$[\{Cu(oatu)_3\}_2SO_4]$	473	30·15	1·176	72·09	$0·468 . 10^6$
$[\{Cu(ocptu)_3\}_2SO_4]$	483	52·19	2·459	91·02	$0·443 . 10^8$

FIG. 1

Pyrolysis curve weight *vs* temperature of *o*-tolylthiourea complex
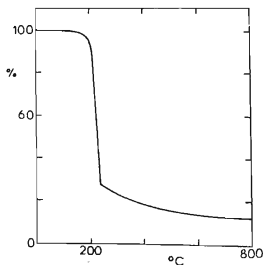
composition temperature for assessing the thermal stability order. Then, this order becomes

$$\left[\{Cu(oatu)_3\}_2SO_4\right] \approx \left[\{Cu(ptu)_3\}_2SO_4\right] > \left[\{Cu(ottu)_3\}_2SO_4\right] >$$
$$> \left[\{Cu(ocptu)_3\}_2SO_4\right].$$
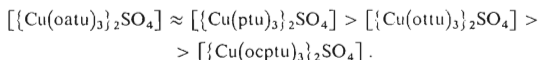
The lowest stability of *o*-chlorophenylthiourea complex may be attributed to the electron withdrawing substituent chlorine on the phenyl group. In spite of the electron releasing substituents methyl and, methoxy, *o*-tolyl and *o*-anisylthiourea complexes are not much more stable than the complex of phenyl thiourea. This may be because of the substitution in *ortho* position which invokes steric hindrance in the complex. A perusal of Table IV indicates that the *o*-tolylthiourea complex lost its weight very rapidly and seems to be the least stable' complex. This observation and the deshielding of NH protons suggest coordination in this complex through the substituted nitrogen.

From our investigations we infer that in the Cu(I) complexes of studied monoaryl-thioureas, the coordination of metal ion occurs with the substituted nitrogen atom of thioureas. The complexes were found not to be polymeric in nature unlike the Co(II) and Ni(II) complexes with the same ligands[30], which were polymeric. This may be due to the less coordination number of Cu(I) in comparison with Co(II) and Ni(II).

REFERENCES

1. Lane T. J., Yamaguchi A., Quagliano J. V., Ryan T. A., Mizushima S.: J. Amer. Chem. Soc. *81*, 3824 (1959).
2. Carlin R. L., Holt jr, S. L.: Inorg. Chem. *2*, 849 (1963).
3. Cotton F. A., Faut O. D., Mague J. T.: Inorg. Chem. *3*, 17 (1964).
4. Puglisi C., Levitus R.: J. Inorg. Nucl. Chem. *29*, 1069 (1967).
5. Gosavi R. K., Agarwala U., Rao C. N. R.: J. Amer. Chem. Soc. *89*, 235 (1967).
6. Piovesana O., Furlani C.: J. Inorg. Nucl. Chem. *32*, 879 (1970).
7. Prasad C. S. G., Banerji S. K.: J. Inorg. Nucl. Chem. *38*, 1387 (1976).
8. Babykutty P. V., Prabhakaran C. P., Anantraman R., Nair C. G. R.: J. Inorg. Nucl. Chem. *39*, 913 (1977).
9. Satpaty K. C., Mishra H. P., Mahana T. D.: Indian J. Chem. *17A*, 303 (1979).
10. Gattegno D., Giuliani A. M.: J. Chem. Soc. Dalton Trans. *167*, 1646 (1973).
11. Eaton D. R., Zaw K.: J. Inorg. Nucl. Chem. *38*, 1007 (1976).
12. Akaiwa H., Kawamoto H., Abe M.: J. Inorg. Nucl. Chem. *34*, 1763 (1972).
13. Farran R., House J. E.: J. Inorg. Nucl. Chem. *34*, 2119 (1972).
14. Zasko J., Varhelyi Cs., Kekedy E.: J. Inorg. Nucl. Chem. *28*, 2637 (1966).

15. Jóna E., Šramko T.: Chem. Zvesti 20, 569 (1966).
16. Spitsyn V. I., Kolli I. D.: Russian J. Inorg. Chem. 9, 54 (1964).
17. Bailey R. A., Tangredi W. J.: J. Inorg. Nucl. Chem. 38, 2221 (1976).
18. Organic Synthesis, Robjohn N. (Ed.): Coll. Vol. 4, 180 (1964).
19. Palmer W. G.: *Experimental Inorganic Chemistry*, p. 132. Cambridge University Press, Cambridge 1965.
20. Emeleus H. J., Anderson J. S.: *Modern Aspects of Inorganic Chemistry*, p. 205. Routledge Kegan Paul Ltd., London 1961.
21. Morgan H. H.: J. Chem. Soc. 1923, 2901.
22. Rosenheim J., Loewenstamm I.: Z. Anorg. Allg. Chem. 34, 62 (1903).
23. Morgan H. H., Burstall K.: J. Chem. Soc. 1930, 143.
24. Spacu A., Murgalescu Y.: Chem. Zentralbl., i. 3422, ii. 535 (1931); 1426 (1931).
25. Stewart W. E., Siddall T. H.: Chem. Rev. 70, 517 (1970).
26. Kumler W. D., Fohlen G. M.: J. Amer. Chem. Soc. 64, 1944 (1942).
27. Swaminathan K., Irving H. M. N. H.: J. Inorg. Nucl. Chem. 26, 1291 (1964).
28. Bajpai A., Mishra D. D.: Jabalpur University Science J. 1, 9 (1982).
29. Nakamoto K., Fujita J., Tanaka S., Kobayashi M.: J. Amer. Chem. Soc. 79, 4904 (1957).
30. Bajpai A., Mishra D. D., Bajpai U. D. N.: J. Macromol. Sci.-Chem. A 19 (6), 813 (1983).
31. Fuoss R. M., Salyer I. O., Wilson H. S.: J. Polym. Sci. A-2, 3147 (1964).