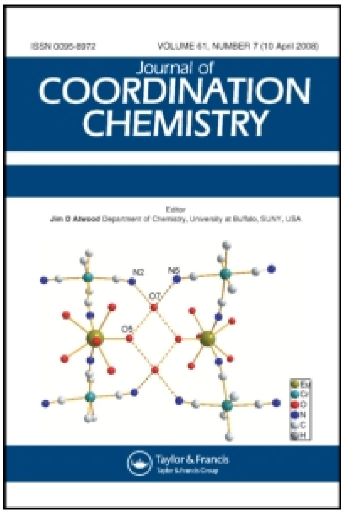

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

BASE HYDROLYSIS OF ISO-THIOCYANATOPENTAAMMINE COMPLEXES OF COBALT(III), CHROMIUM(III) AND RHODIUM(III) IN AQUEOUS-ORGANIC MIXED SOLVENTS

M. n. Bishnu[a]; B. Chakravarti[a]; R. N. Banerjee[a]; D. Banerjea[a]
[a] Department of Chemistry, Inorganic Chemistry Division, University College of Science, Calcutta, India

To cite this Article Bishnu, M. n. , Chakravarti, B. , Banerjee, R. N. and Banerjea, D.(1983) 'BASE HYDROLYSIS OF ISO-THIOCYANATOPENTAAMMINE COMPLEXES OF COBALT(III), CHROMIUM(III) AND RHODIUM(III) IN AQUEOUS-ORGANIC MIXED SOLVENTS', Journal of Coordination Chemistry, 13: 1, 63 — 69
To link to this Article: DOI: 10.1080/00958978308079755
URL: http://dx.doi.org/10.1080/00958978308079755

J. Coord. Chem., 1983, Vol. 13, pp. 63–69
0095-8972/83/1301-0063 $18.50/0

BASE HYDROLYSIS OF ISO-THIOCYANATOPENTAAMMINE COMPLEXES OF COBALT(III), CHROMIUM(III) AND RHODIUM(III) IN AQUEOUS-ORGANIC MIXED SOLVENTS

M.N. BISHNU, B. CHAKRAVARTI, R.N. BANERJEE and D. BANERJEA†

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

(Received July 21, 1982; in final form February 20, 1983)

In the base hydrolysis of the title complexes in aqueous-organic solvent media (water-ethanol and water-acetone) to the corresponding hydroxo-complexes the observed rate law is in accord with the expression:

$$[OH^-]/k_{obs} = [OH^-]/k + 1/kK.$$

The observed K values (3.5 to 26 M^{-1} at 25°) and the nature of their solvent dependence suggest the formation of an ion-pair in a pre-equilibrium involving the substrate complex and OH^- ion, and not of a conjugate base. Rate constants (k) for the transformation of the ion-pair to the product increase with increased proportions of the organic component in the solvent. The nature of the dependence of k on different solvent parameters indicates significant associative character with OH^- ion acting as the attacking nucleophile. Activation enthalpy, $\Delta H^{\neq}$, decreases with ethanol concentration; this along with the observed large positive slopes of the log k *vs* 1/D plots rule out the possibility of H_2O acting as the attacking nucleophile. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ corresponding to k in different solvent compositions for a particular complex are linearly correlated. A common mechanism appears plausible for all the complexes in which bond breaking and bond making are synchronous but their relative contributions are different giving a relatively more associative character to the cobalt(III) and rhodium(III) systems compared to the chromium(III) system. This view is supported by the magnitudes of the slopes of the log k *vs* 1/D, and log k *vs* Y plots. The dissociation of the M–NCS bond is probably solvent assisted due to solvation of the departing ligand as indicated by the linear dependence of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ on different solvent parameters.

INTRODUCTION

Investigations of the influence of solvent on reaction rates of coordination complexes is an active field,[1] because correlation of reaction rates with various solvent parameters can give important mechanistic information.[2–5] Acidopentaammine complexes of Co(III) are generally believed to react by dissociative pathways, while an associative activation is commonly ascribed to the reactions of similar Cr(III) and Rh(III) complexes.[6] However, exceptions are not rare[7,8] and in the course of studies[9–11] on the base hydrolysis of the title complexes in aqueous media it was observed that none of these complexes react by a purely dissociative path.

It was therefore thought worthwhile to study the base hysrolysis of the title complexes in water-ethanol and water-acetone mixtures of various compositions to check the correctness of our previous mechanistic conclusions and the utility of such solvent variation studies in the interpretation of mechanism. A few such solvent variation studies[12] have so far dealt with the base hydrolysis of coordination complexes.

---

† To whom correspondence should be addressed.

EXPERIMENTAL

Materials and Reagents.

The isothiocyanatopentaammine complexes were synthesised by known methods[13-15] and their purity was checked by elemental analysis and their electronic spectra.[15,16] All the solvents employed including water were distilled twice before use; other chemicals used were of reagent grade.

Apparatus and Procedure.

The details of the kinetic procedure are the same as those described elsewhere[10,11]; the rate of release of the thiocyanate ion was monitored spectrophotometrically by its colour formation with Fe(III) perchlorate reagent.[10] The absorption measurements were made using a Carl-Zeiss (VSU-2P) spectrophotometer and stoppered quartz cells of suitable path length. Observed A_∞ values were found to be somewhat dependent on the solvent composition and were therefore evaluated in separate experiments for each of the solvent compositions. During the course of the measurements (up to *ca* 50% of the reaction) there was apparently no loss of ammonia and hence the product was $[M(NH_3)_5(OH)]^{2+}$ in each case.

Results and Discussion

Under the experimental conditions, the dependence of the pseudo-first-order rate constants (k_{obs}) of the base hydrolysis reactions of the title complexes on alkali concentration in all cases nicely fits the linear relation (*1*).

$$[OH^-]/k_{obs} = [OH^-]/k + 1/kK. \qquad (1)$$

TABLE I

Rate constants (k) for the base hydrolysis of $[M(NH_3)_5(NCS)]^{2+}$ in water-organic solvent mixtures.

% Organic solvent[b] (v/v)	10^5 k, s^{-1} [a]								
	M = Cr(III)[c]			M = Co(III)[d]			M = Rh(III)[e]		
	30°	35°	40°	25°	30°	35°	50°	55°	60°
5	0.71 (1.06)	1.30	2.45	6.00	11.7	23.2			
10	0.02 (1.48)	1.84	3.40	9.00	17.2	33.3	1.65	3.00	5.58
15	1.27 (1.97)	2.18	3.97	12.3	23.3	41.8	2.55	4.57	8.20
20	1.45 (2.55)	2.53	4.38	16.7	30.0	52.7	3.33	5.68	9.75
25	1.65 (3.23)	2.79	4.63	23.6	41.7	66.7	4.10	6.95	11.6
30	2.10 (3.97)	3.30	5.38	32.1	52.0	83.0	5.00	8.12	13.2

[a] Maximum standard deviation in k is ± 5%. [b] Ethanol, except the values in parentheses which are for acetone. [c] Complex, 0.002 M; $[OH^-]$, 0.01 - 0.25 M. [d] Complex, 0.002 M; $[OH^-]$, 0.01 - 0.06 M. [e] Complex, 0.001 M; $[OH^-]$, 0.015 - 0.20 M.

TABLE II
Equilibrium constants, K, for formation of intermediates (ion-pairs) in the base hydrolysis of $[M(NH_3)_5(NCS)]^{2+}$.

% Organic solvent[a] (v/v)	K,M^{-1}										
	M = Cr(III)				M = Co(III)			M = Rh(III)			
	25°[b]	30°	35°	40°	25°	30°	35°	25°[b]	50°	55°	60°
5	11.0	12.9 (8.4)	15.8	18.2	13.7	15.9	18.6				
10	12.6	14.9 (10.5)	19.9	22.3	15.9	19.4	22.2	3.5	7.2	11.0	14.7
15	14.8	16.5 (12.2)	21.2	26.2	19.5	21.1	26.7	5.1	9.6	15.3	16.3
20	17.4	18.0 (14.7)	26.3	34.5	20.8	22.2	30.2	6.9	12.2	17.4	20.1
25	19.5	21.7 (18.7)	29.0	40.0	23.6	25.0	35.7	9.5	15.1	24.0	27.0
30	22.9	24.6 (19.5)	35.7	47.7	26.0	29.7	40.0	13.2	18.5	31.5	37.0

[a]Ethanol, except the values in parentheses which are for acetone. [b]Extrapolated values.

suggesting the formation of an intermediate in a pre-equilibrium (equilibrium constant, K) followed by its transformation into the product in a rate determining step (rate constant, k).

Both k and K values have been evaluated graphically using equation (*1*) under various experimental conditions (Tables I and II). From the temperature dependence of k under otherwise identical conditions, the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for these reactions have been evaluated in different solvent mixtures using the Eyring equation and a least squares method (Table III).

The values of K for all the three complexes are practically independent of the nature of the central metal atom, and in different solvent media lie within the range 3.2 - 26 M^{-1} at 25° which is in the range of values expected for ion-pair formation in these systems.[6,11]

TABLE III
Activation parameters[a] for the base hydrolysis of $[M(NH_3)_5(NCS)]^{2+}$.

% Ethanol (v/v)	M = Cr(III)		M = Co(III)		M = Rh(III)	
	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$
5	95.3 ± 1.5	−30.5 ± 5.0	99.9 ± 1.6	8.4 ± 5.8		
10	92.8 ± 1.2	−35.1 ± 4.0	97.0 ± 2.0	2.1 ± 6.1	104.9 ± 2.3	−13.8 ± 8.0
15	87.8 ± 2.0	−50.2 ± 7.0	90.7 ± 1.1	−16.7 ± 3.6	99.9 ± 1.2	−25.5 ± 4.1
20	83.6 ± 1.5	−63.1 ± 4.8	85.7 ± 1.9	−30.9 ± 6.5	94.0 ± 1.2	−41.0 ± 3.7
25	79.0 ± 1.6	−77.3 ± 5.3	77.3 ± 2.5	−56.4 ± 7.9	90.3 ± 0.8	−51.4 ± 3.3
30	73.1 ± 0.4	−94.9 ± 1.6	70.6 ± 1.1	−76.3 ± 3.5	82.8 ± 1.6	−73.1 ± 5.4

[a]$\Delta H^{\neq}$ units are kJ mol^{-1}, $\Delta S^{\neq}$ units are J K^{-1} mol^{-1}.

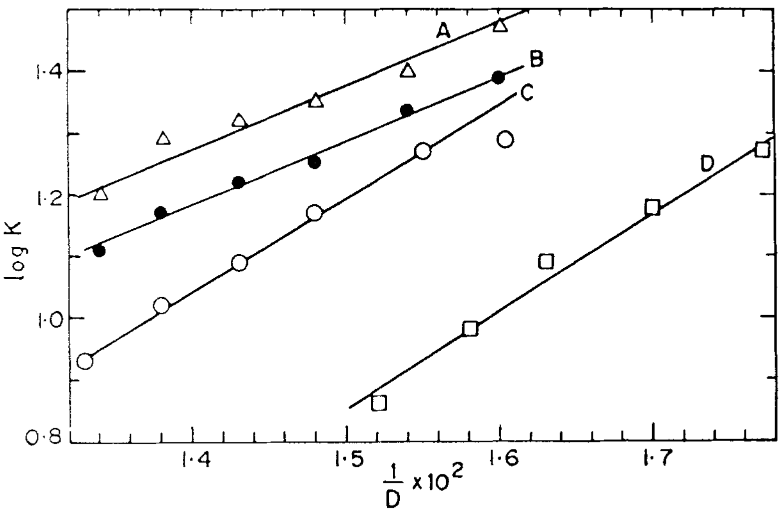

FIGURE 1 Log k *vs* 1/D plots: (A), for Co(III) at 30° in water-ethanol mixtures; (B), for Cr(III) at 30° in water-ethanol mixtures; (C), for Cr(III) at 30° in water-acetone mixtures; (D), for Rh(III) at 50° in water-ethanol mixtures.

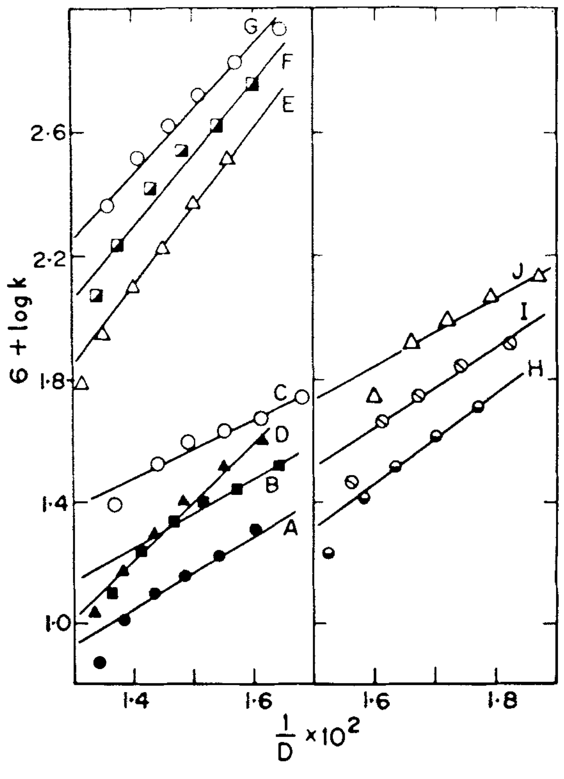

FIGURE 2 Log k *vs* 1/D plots: (A), (B), (C): for Cr(III) at 30°, 35° and 40° in water-ethanol mixtures; (D); for Cr(III) at 30° in water-acetone mixtures; (E), (F), (G): for Co(III) at 25°, 30° and 35° in water-ethanol mixtures; (H), (I), (J): for Rh(III) at 50°, 55° and 60° in water-ethanol mixtures.

Thus the intermediate is an ion-pair and not a conjugate base, because in the latter case the equilibrium constant is expected to be much smaller (since the acidity of the ammine proton in such complexes is very weak with $pK_a \approx 14$).[6] The nature of dependence of K on solvent composition also agrees with ion-pair formation; an increase in the organic component in the solvent increases K, and plots of log K *vs* 1/D (D = the dielectric constant of the medium)[17] are perfectly linear in all the cases (Fig. 1).

The rate constants are also strongly influenced by the nature of the solvent and solvent compositions. Plots of log k *vs* 1/D in all the cases studied were found to be linear with large positive slopes (in H_2O-EtOH at 30°; Cr, 120; Co, 233; Rh, 212, using extrapolated k values at 30°; see Fig. 2).

This result rules out a purely dissociative mechanism and suggests a sort of associative activation in the transformations of the intermediate ion-pairs to the products. Similar conclusions are drawn from the observed dependence of k on other interrelated solvent parameters like $(D - 1)/(2D + 1)$, the Y value[18] (slopes of log k *vs* Y plots in H_2O-EtOH at 30°, see Fig. 3: Cr, −0.53; Co, −0.84; Rh, −0.93), the Z value[19] and the E_T value.[20]

Regarding the nature of the attacking nucleophile in the rate determining step, involvement of OH^- appears more plausible than H_2O from the present experimental results, since $\Delta H^{\neq}$ decreases with increasing concentration of ethanol (Table 3) in water-ethanol mixtures which rules out H_2O as the attacking nucleophile. Also, for an associative activation involving an ionic complex and an uncharged water molecule, the slope of the log k

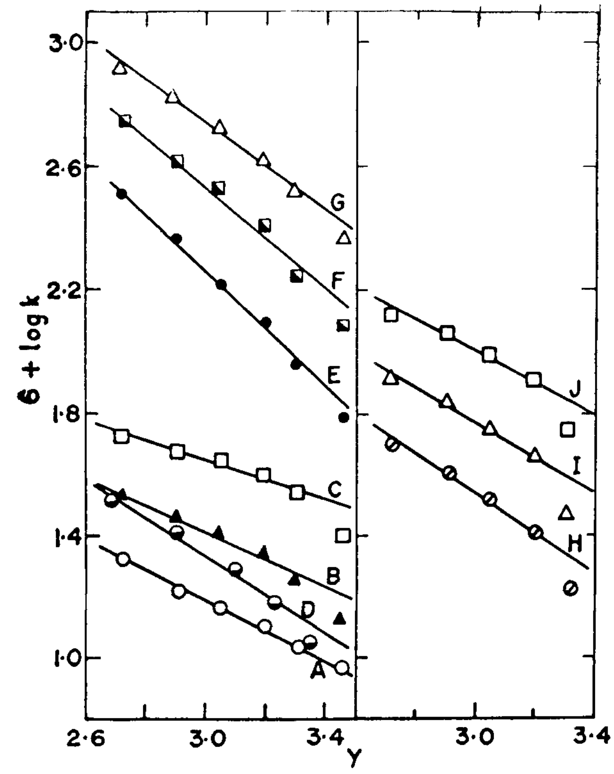

FIGURE 3 Log k *vs* Y plots: (A), (B), (C): for Cr(III) at 30°, 35° and 40° in water-ethanol mixtures; (D), for Cr(III) at 30° in water-acetone mixtures; (E), (F), (G): for Co(III) at 25°, 30° and 35° in water-ethanol mixtures; (H), (I), (J) for Rh(III) at 50°, 55° and 60° in water-ethanol mixtures.

vs 1/D plot should be a small quantity.[21] If M-NCS bond dissociation is also significant and synchronous with M-OH$_2$ bond formation, its effect should make the slope negative. Hence the observed large positive slopes of log k *vs* 1/D plots also rule out H$_2$O as the attacking nucleophile. However, for an associative activation involving a significant degree of M-OH bond formation in reaching the transition state, the slopes of the log k *vs* 1/D plots should be positive[22] and this should decrease with an increase of temperature as has actually been observed (Fig. 2). Involvement of synchronous M-NCS bond dissociation, however, may reduce the magnitude of the positive slope due to M-OH bond formation since a decrease in the dielectric constant influences these processes in an opposite manner.[21] At any temperature, the observed sequence of slopes of the log k *vs* 1/D plots (Co > Rh ≫ Cr) (*loc. cit.*) is therefore suggestive of a significant difference in the relative degree of M-NCS bond breaking (significantly higher for Cr(III)) and M-OH bond making (considerably more pronounced for Co(III) and Rh(III)) in the three different cases studied. This is in agreement with what has been inferred earlier for these reactions in aqueous solution.[9-11] Slopes of the log k *vs* Y plots are significantly more negative for the Co(III) and Rh(III) complexes than for the Cr(III) complex, thus supporting this view. Good isokinetic relationships ($\Delta H^{\neq}$ *vs* $\Delta S^{\neq}$ plots are linear; correlation coefficients *ca* 0.998) have been observed for each of the three complexes in water-alcohol mixtures of different composition (Fig. 4).

Experimental evidences have been adduced[23] in fairly recent years that, depending on the nature of the system, I_d or I_a mechanisms may operate both for Co(III) and Cr(III). Base hydrolysis of $[Cr(NH_3)_5(N_3)]^{2+}$ involves a dissociative[24] process, but that of $[Co(NH_3)_5(S_2O_3)]^+$ is associative[25] in character.

Both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are linearly related with the various solvent parameters (correlation coefficients *ca* 0.996) which suggests significant solvent participation as well. It is likely that the loss of SCN$^-$ is assisted by solvation which appears to increase with an increase in ethanol concentration (alkali thiocyanates have a high solubility in alcohol indicating that thiocyanate ion is highly solvated in alcohol also). The more negative value

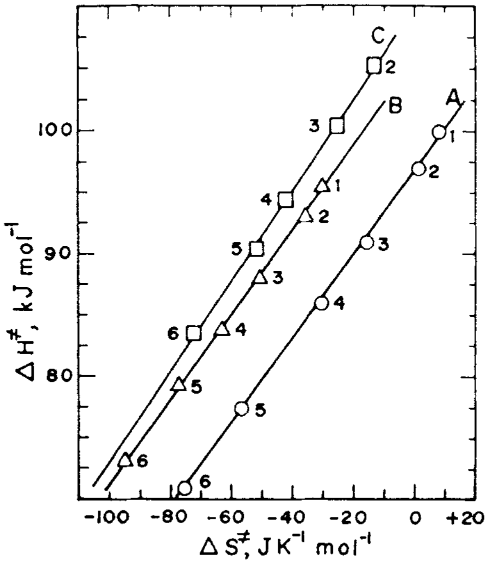

FIGURE 4 $\Delta H^{\neq}$ *vs* $\Delta S^{\neq}$ plots: (A), (B), (C): for Co(III), Cr(III) and Rh(III) reactions; (1) - (6): Aqueous-ethanol media containing 5, 10, 15, 20, 25 and 30 percent (v/v) ethanol respectively.

of $\Delta S^{\neq}$ (Table 3) observed for the Cr(III) complex agrees with a greater degree of M-NCS bond dissociation and concurrent solvation of the SCN^- ion.

The k values are more sensitive to solvent composition when acetone is the co-solvent. The rate is also faster in the water-acetone solvent system even at the same composition at which water-acetone and water-alcohol media are practically iso-dielectric.

ACKNOWLEDGEMENTS

The investigations have been carried out with financial assistance and facilities provided by Calcutta University. This and the award of research scholarships to two of us (M.N.B. and B.C.) are gratefully acknowledged.

REFERENCES

1. J. Burgess, Inorganic Reaction Mechanism Specialist Periodic Report, Chemical Society (London), **1**, 163 (1971); S. Asperger, *Inorg. Chim. Acta.*, **40**, (1980); E. Buncel, *Inorg. Chim. Acta.*, **40**, 16 (1980).
2. M.J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, **4**, 55 (1975); M.J. Blandamer and J. Burgess, Pure Appl. Chem., **51**, 2087 (1979); C.H. Langford and V.S. Shastri, in Reaction Mechanism in Inorganic Chemistry, Vol. 9, series 1, Ch. 6, (Ed.) M.L. Tobe, Butterworths, London (1971); E.S. Amis, in Solvent Effects on Reaction Rates and Mechanism, Academic Press, New York (1966); P.J. Staples, *Coord. Chem. Rev.*, **11**, 277 (1973).
3. C.F. Wells, *J. Chem. Soc. Farad. I*, **73**, 1851 (1977) and references therein; A.V. Ablov and N.M. Samus, *Coord. Chem. Rev.*, **17**, 253 (1975); *ibid.*, **28**, 177 (1979).
4. C.W. Elgy and C.F. Wells, *J. Chem. Soc. Dalton*, 2405 (1980).
5. J. Burgess, *J. Chem. Soc. (A)*, 2703 (1970).
6. F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd Edn., John Wiley and Sons, New York (1967); D. Banerjea, Fundamental Principles of Inorganic Chemistry, Sultan Chand and Sons, New Delhi, (1978).
7. A. Dhur, S. Das, R.N. Banerjee and D. Banerjea, *Trans. Met. Chem.*, **7**, 125 (1982).
8. A.K. Basak and C. Chatterjee, *Trans. Met. Chem.*, **5**, 212 (1980).
9. D. Banerjea, and T.P. Dasgupta, *J. Inorg. Nucl. Chem.*, **28**, 1667 (1966).
10. D. Banerjea and C. Chatterjee, *Z. anorg. allgm. Chem.*, **361**, 99 (1968).
11. C. Chatterjee, P. Choudhury and D. Banerjea, *Indian J. Chem.*, **8**, 1123 (1970).
12. S.C. Chan and K.Y. Hui, *J. Chem. Soc. (A)*, 1941 (1968); *ibid.*, 2103 (1967); M. Birus, W.L. Reynolds, M. Pribanic and S. Asperger, *Croat. Chem. Acta*, **47**, 561 (1975).
13. A.W. Adamson and R.G. Wilkins, *J. Amer. Chem. Soc*, **76**, 3379 (1954); for evidence of Cr-N bonding see J.C. Bailar, *J. Amer. Chem. Soc.*, **81**, 6412 (1959).
14. A Werner and N. Gosling, *Ber.*, **36**, 2380 (1903); Inorganic Synthesis, Vol. IV p. 174, J;C. Bailar, (Ed.), McGraw Hill, New York (1953); A. Werner and H. Müller, *Z. anorg. Chem.*, **22**, 101(1900).
15. H.H. Schmidtke, *Z. physik. Chem. (Neue Folge)*, **45**, 305 (1965).
16. C.H. Langford and W.R. Muir, *J. Amer. Chem. Soc.*, **89**, 3141 (1967).
17. G. Akerlöf, *J. Amer. Chem. Soc.*, **54**, 4125 (1932).
18. A.H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).
19. E.M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).
20. K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlman, *Annalen*, **661**, 1 (1963).
21. V.D. Panasyuk and A.V. Arkharov, *Russ. J. Inorg. Chem.*, **13**, 406 (1968); V.V. Udovenko, L.G. Reiter and E.P. Shkurman, *Russ. J. Inorg. Chem.*, **18**, 1296 (1973).
22. V.D. Panasyuk and L.G. Reiter, *Russ. J. Inorg. Chem.*, **11**, 329 (1966).
23. T.W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974); T. Ramaswami and A.G. Sykes, *Chem. Comm.*, 378 (1976).
24. C. Chatterjee and P. Chaudhuri, *Indian J. Chem.*, **9**, 1132 (1971).
25. D. Banerjea and T.P. Das Gupta, *J. Inorg. Nucl. Chem.*, **27**, 2617 (1965); D. Banerjea, *J. Chem. Ed.*, **44**, 485 (1967).