

CHAPTER VI
Nitration reactions of Cu(II) mixed
ligand imine complexes

In the earlier chapters we have made an attempt to show the extent of π interaction in M- β -diketone complexes in mixed ligand systems. It has been shown by several workers that the acetylacetonate complexes in several ways behave like aromatic systems. Collman and associates^{1,2} have carried out extensive investigation of the chemistry of acetylacetonate anion when complexed to a metal. They found that the ring behaves similar to aromatic compounds. Specially they find that, "The central hydrogen atom on these chelate rings can be replaced by several groups. Under apparently electrophilic conditions--- Halogenation, Thiocyanation, Arylsulfonylation, Nitration, Friedel Crafts Acylation, Formylation, Chloromethylation and Dimethylamino-methylation have been realised". These studies unambiguously show that chemically speaking the chelate rings are aromatic.

Singh and Sahai³⁻⁸ have recently reported experiments of interest to show the relation between metal acetylacetonates and benzene type molecules. The 3-nitro derivative in metal-acetylacetonates can be reduced to 3-amino which in turn can be diazotised.⁹ Halogenation of bis(dithioacetylacetonate) complexes of Co(III) and Ni(II) have been carried out by Faruhoshi Akiko.¹⁰ Rukhadz and coworkers¹¹ have reported bromination and hydroxymethylation of Cu(II) hydroxyazo-methines.

Halogenation has been carried out on the mixed Cr(III) complexes containing acetylacetonate.¹² Tamaki Motonari have carried out the nitration reactions on N,N' -ethylene-bis-salicylaldehyde¹³ $M(II)$ -Acetylacetonate, salicylaldehyde and

methylsalicylate compounds of Co(II), Ni(II), Zn(II), Fe(II), Ca(II), K, and Na with pyridine, piperidine or morpholine as additional ligands reacted with SO_2 , Cl_2 , Br_2 and O_2 to give the free dihalogenated compounds.¹⁴ Kasahara Akira¹⁵ has carried out the halogenation of Pd(II) complexes of β -oxoamines. Sen has carried out¹⁶ the bromination of some metal acetylacetonates. Substitution reactions under electrophilic substitution reaction conditions have been attempted¹⁷ on the binary metal complexes of salicylaldehyde to give the 3,5-tetra substituted compounds. Acylation of Cu(II) β -diketonates have been carried out.¹⁸ Nitration of Be(II) chelates of substituted acetoacetamides have been carried out.¹⁹ Bromination reactions involving Ni(II) and Cu(II) complexes of Schiff base derivative of acetylacetone have been reported recently by Lindoy and coworkers.²⁰ In our laboratory nitration reactions have been carried out²¹ on mixed ligand complexes CuLL' where $\text{LH} = \text{salicylaldehyde}$ and $\text{L}'\text{H} = 2\text{-hydroxyacetophenone}$ or 3,4,5-methyl substituted 2-hydroxyacetophenone.

Different nitrating agents like N_2O_4 , a mixture of copper nitrate, beryllium nitrate in acetic anhydride^{15,16,22} or $\text{N}_2\text{O}_4 \cdot \text{BF}_3$ ²³ have been used for bringing the nitration reactions. The conditions of nitration have been maintained such that the ligand does not break from the complex. Nitration reactions have been mostly carried out in case of Cu(II) complexes because they are more stable and the ligand does not break easily. Acetyl nitrate has been used as the nitrating agent. It is formed in situ by the reaction of copper nitrate with acetic anhydride. It has been used for many reactions^{15,17,20} and in case of coordinated ligands the

reagent seems to have many advantages over the other strong nitrating agents like N_2O_4 , HNO_3 and H_2SO_4 , which being stronger reagents, cause decomposition of the Schiff base complexes.

The present study consists of nitration reactions carried over Cu(II) mixed ligand complexes described in the previous chapter.

Experimental :

Materials used :

Acetic anhydride (BDH), copper nitrate trihydrate (Riedel, pure Germany), sodium acetate crystals (Pfizer) were used.

Nitration reaction has been carried out on the following mixed ligand complexes :

1. (Salicylideneamino-acetylacetonato)Cu(II)
2. (Salicylideneamino-benzoylacetonato)Cu(II)
3. (Salicylideneamino-dibenzoylmethanato)Cu(II)
4. 1-(2-hydroxyphenyl)ethylideneamino-acetylacetonato)Cu(II)
5. 1-(2-hydroxy m-tolyl)ethylideneamino-acetylacetonato)Cu(II)

The mixed Schiff base complexes (0.0016) and acetic anhydride (10 ml.) were taken in a 250 ml. Erlenmeyer flask fitted with a calcium chloride drying tube and stirred magnetically over an ice bath for 15 minutes. Powdered $Cu(NO_3)_2 \cdot 3H_2O$ (0.0024) mole was added in small portions over a period of 30 minutes. The ice bath was removed after 5-6 hours. Longer refluxing period was required for BA, DBM and methyl substituted 2-hydroxyacetophenone. The resulting green

coloured slurry was decomposed by pouring into 100 ml. of ice cold water containing sufficient amount of sodium acetate and stirring for an hour. The precipitate obtained was filtered under suction, washed with water, then with ethanol and recrystallised. The compounds were analysed for metal and nitrogen contents. Analytical data are given in the table VI 1.

T.L.C. measurements :

TLC was carried out on silica gel G (Sichem) using a mixture of chloroform and ether.

Conductivity measurements :

The conductance measurements were carried out in ethanol solutions. They are found to be non-conducting.

Magnetic measurements :

Magnetic susceptibilities were determined at room temperature ($\sim 30^{\circ}\text{C}$) using Guoy balance. The magnetic moment values have been shown in table VI 1.

Visible spectral studies :

The solubility of the nitrated compounds is very low in all the solvents, and hence absorption spectra could not be obtained. It would have been interesting to get the reflectance spectra of the compounds. The author regrets the non availability of the facilities to get it.

IR spectral studies :

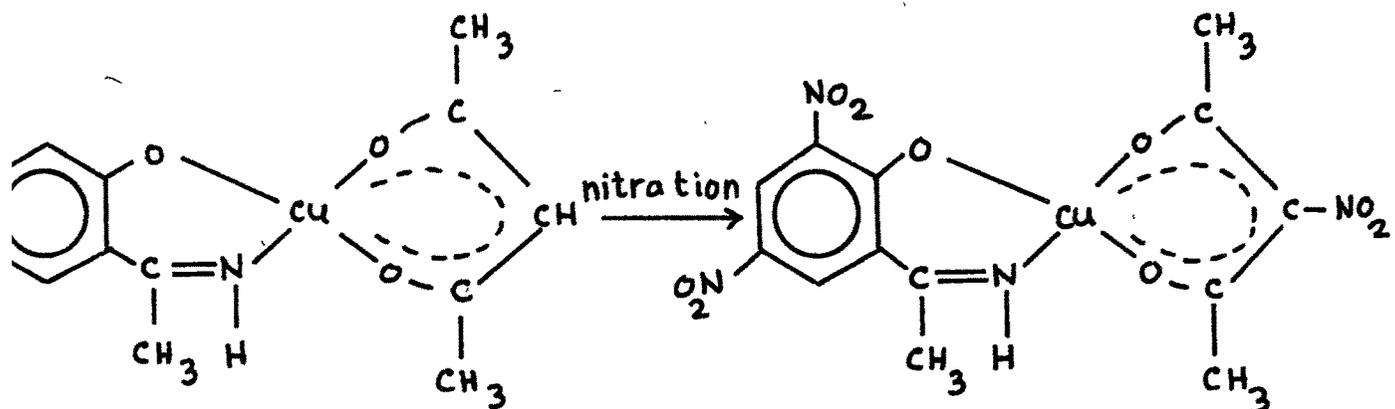
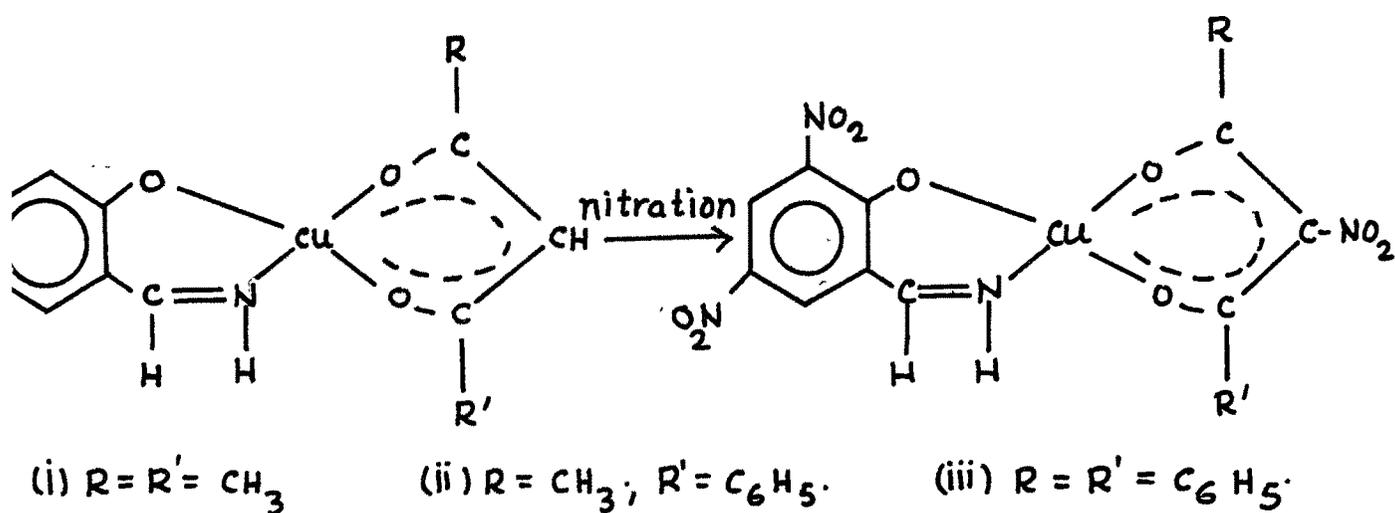
The IR spectra of the compounds were obtained in the form of KBr discs. The characteristic bands obtained are as follows :

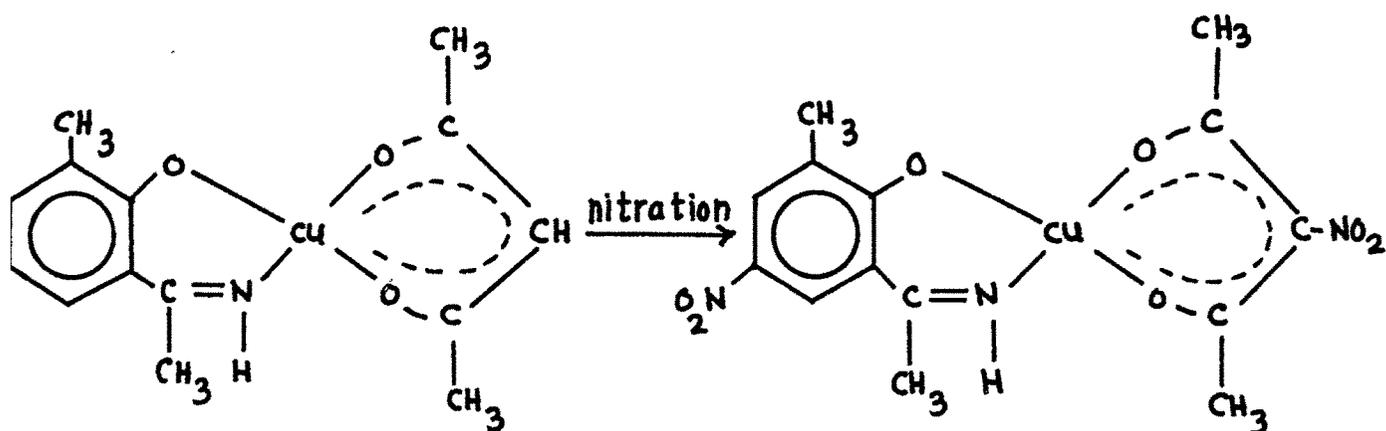
<u>Compound</u>	<u>Characteristic bands cm⁻¹</u>		
1. (3,5-dinitrosalicylideneamina- to-3-nitroacetylacetonato)Cu(II)	~3300s	~3080w	~2920w
	~2850w	~1600s	~1570s
	~1530m	~1500w	~1465m
	~1445s	~1415s	~1350s
	~1240s	~1100s	~960s
	~930s	~840m	~805w
	~770s	~745s	~720s.
	2. (3,5-dinitrosalicylideneamina- to-3-nitrobenzoylacetono)Cu(II)	~3300s	~3080s
~1600s		~1570s	~1540s
~1490s		~1465m	~1440s
~1420m		~1350s	~1240s
~1220w		~1185w	~1100s
~960s		~925s	~850s
~800s		~770s	~750s
~720s		~690w.	
3. (3,5-dinitrosalicylideneamina- to-3-nitro-dibenzoylmetanato) Cu(II)	~3300s	~3080w	~2920w
	~1650s	~1600s	~1590s
	~1540w	~1490w	~1450s
	~1360s	~1325s	~1300s
	~1240s	~1190w	~1175s
	~1140s	~1100w	~1025m
	~1000s	~940m	~900s
	~850m	~835s	~805m
4. [1-(2-hydroxy,3,5-dinitrophenyl- ethylideneaminato,3-nitroacetyl- acetonato)]Cu(II)	~3300s	~3080w	~2920w
	~1600s	~1570s	~1530s
	~1450-1470s	~1405m	~1340s
	~1290w	~1250w	~1230m
	~1120s	~1040s	~1005w
	~940s	~930s	~890w
	~870s	~850m	~830w
	~790w	~780s	~745s
	~710s	~655w.	

5. [1-(2-hydroxy-5-nitro-m-tolyl- ethylideneaminato-3-nitroacetyl- acetonato)]Cu(II)	✓3300s	✓3080w	✓2920w
	✓1600s	✓1565s	✓1495s
	✓1440s	✓1410w	✓1380w
	✓1320s	✓1240m	✓1220w
	✓1130s	✓1035w	✓995s
	✓910s	✓830s	✓770s
	✓750s	✓690w.	

Results and Discussion :

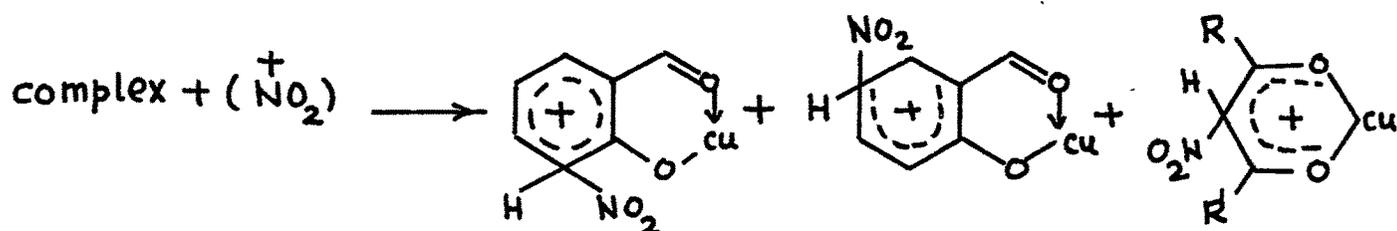
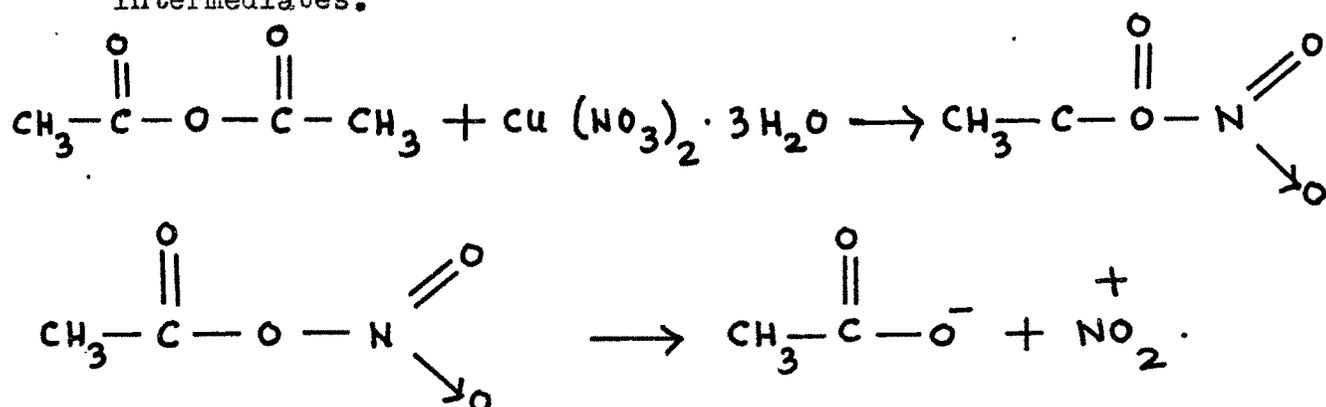
In the present mixed ligand imine Schiff base complexes, the substitution of a nitro group leads to a trinitro compound;





except in case of mixed Schiff base complex containing 2-hydroxy-3-methyl acetophenone, where a dinitro compound is formed. It is due to the fact that the 3-position is already occupied by the methyl group.

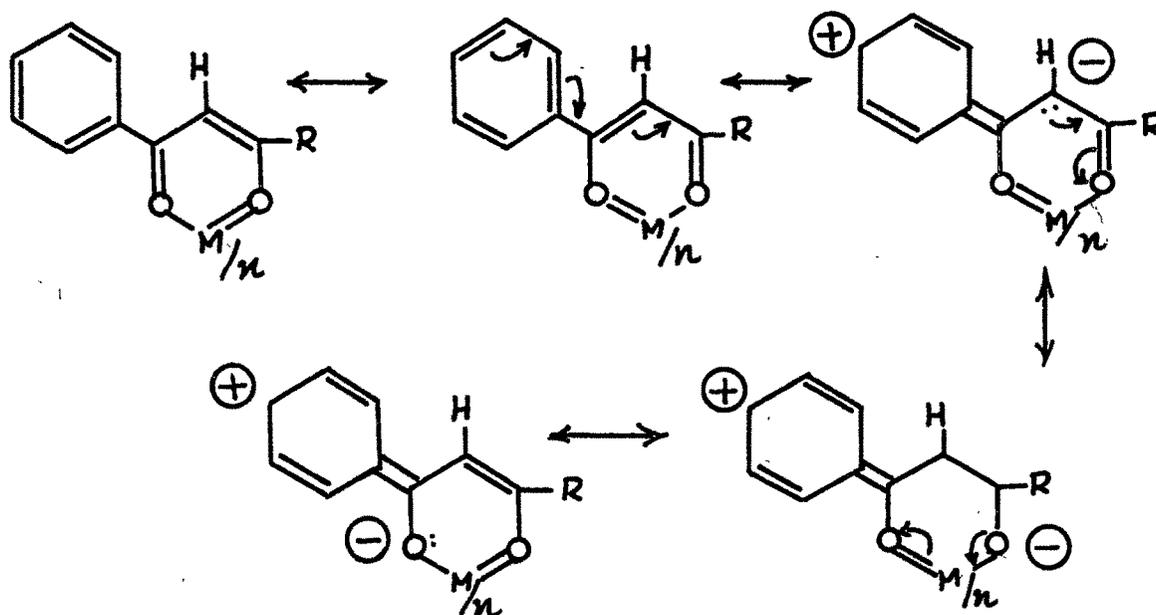
Nitronium ions produced from this reagent act as electrophile to form the resonance stabilised σ complex intermediates.



Removal of a proton from each of these intermediates and further reaction of the ligands with $\ddot{\text{N}}\text{O}_2$ gives the trisubstituted compounds.

In the acetylacetone part only one group can enter as the H atom on the γ -carbon is labile and susceptible to electrophilic substitution. In the salicylaldehyde or 2-hydroxyacetophenone part of the molecule, nitration takes place at 3 and 5 positions rather than 4 and 6 positions. This is due to the ortho, para orienting effect of phenolic oxygen and meta directing effect of $-\text{C}=\text{N}$. Thus orientation of the incoming substituents in the mixed Schiff base complexes are found to be the same as for the uncomplexed salicylaldehyde or 2-hydroxyacetophenone.

In the mixed complexes containing BA and DBM, the electrophilic substitution in the phenyl ring is not favoured.⁸ It is to be expected as the phenyl rings get deactivated; towards attack by electrophilic reagents due to its predominantly electron releasing resonance effect in these systems-



In general the nitration reactions over acetylacetone are faster than benzoylacetone or dibenzoylmethane carrying phenyl derivatives? An increase in electron density at reaction site, because of electron releasing mesomeric effect (-M effect) of phenyl ring, favours reaction, but the steric effect of coplanar phenyl groups at ortho positions to reaction site is of more importance and retards the rate of reactions. In other words the yield decreases and reaction time increases as the methyl group is substituted by the phenyl rings.

The nitrated compounds are non-conducting showing that they are neutral. Thus it is clear that the nitro groups are substituted on the ligands and are not present as the anion.

The nitrated compounds are paramagnetic having magnetic moment corresponding to one unpaired electron. (1.8 to 2.00 B.M.). There is no change in the paramagnetic value of nitrated compound of Cu(II) mixed Schiff base complex from those without nitro substitution.

In the IR spectra of the compounds band in the region $\sim 3400 \text{ cm}^{-1}$ is absent showing that water is absent in these compounds. In the nitrated imine compounds there is a sharp band at $\sim 3300 \text{ cm}^{-1}$ corresponding to N-H stretching frequency. Band $\sim 1620 \text{ cm}^{-1}$ corresponds to C=N of imine linkage. The band at $\sim 1570 \text{ cm}^{-1}$ corresponds to C=O of the diketone. The band $\sim 1450 \text{ cm}^{-1}$ corresponds to C=C stretching frequency. The nitrated compounds show a band $\sim 1510 \text{ cm}^{-1}$ corresponding to asymmetric NO₂ stretching frequency, while that $\sim 1330 \text{ cm}^{-1}$

corresponds to symmetric NO₂ stretch.

In general due to the nitro substitution a large number of the C-H bands disappear. The bands obtained are thus few in number and a general broadening of the bands is observed.²⁴

The disappearance of the C-H in plane bending vibrations at $\sim 1225 \text{ cm}^{-1}$ and appearance of NO₂ stretching vibration bands at $\sim 1330 \text{ cm}^{-1}$ at the same time provides strong evidence for the NO₂ group entering each chelate ring at the carbon atom.

Table VI-1 : Analytical data, electronic spectral band and magnetic moments of nitrated mixed imine Schiff base complexes of Cu(II)

No.	Name of the complex	Analytical data %				λ_{max} in nm	μ_{eff} in B.M.				
		Calculated		Found							
		Cu	C	H	N	Cu	C	H	N		
1	(3,5,dinitrosalicylidene-aminato,3-nitroacetylacetato)Cu(II)	15.23	-	-	13.42	15.01	-	-	13.44	-	1.86
2	(3,5,dinitrosalicylidene-aminato,3-nitrobenzoyl-acetonato)Cu(II)	13.25	-	-	11.68	13.43	-	-	11.74	-	1.82
3	(3,5,dinitrosalicylidene-aminato,3-nitrodibenzoyl-methanato)Cu(II)	11.73	-	-	10.34	11.53	-	-	10.68	-	1.89
4	[1-(2-hydroxy,3,5,dinitro-phenyl)ethylideneaminato,3-nitroacetylacetato]Cu(II)	14.72	-	-	12.98	14.92	-	-	12.88	-	1.93
5	[1-(2-hydroxy,5-nitro-phenyl)ethylideneaminato,3-nitroacetylacetato]Cu(II)	15.95	-	-	7.03	15.73	-	-	7.24	-	1.91

References :

1. Collman, J.P., and Barker, R.H., reported in *Angew. Chem. Intern. Ed. Engl.*, 4, 132 (1965).
2. Barker, R.H., Collman, J.P., and Marshall, R.L., *J. Org. Chem.*, 29, 3216 (1964).
3. Singh, P.R., and Sahai, R., *Aust. J. Chem.*, 20, 649 (1967).
4. Singh, P.R., and Sahai, R., *Inorg. Nucl. Chem. Letters*, 4, 513 (1968).
5. Singh, P.R., and Sahai, R., *Aust. J. Chem.*, 22, 263 (1969).
6. Singh, P.R., and Sahai, R., *Aust. J. Chem.*, 20, 639 (1967).
7. Singh, P.R., and Sahai, R., *Ind. J. Chem.*, 7, 628 (1969).
8. Singh, P.R., and Sahai, R., *Inorg. Chim. Acta.*, 2, 102 (1968).
9. Collman, J.P., and Yamada, M., *J. Org. Chem.*, 28, 3017 (1963).
10. Faruhoshi, A., *Bull. Chem. Soc. Japan.*, 42(1), 260 (1969).
11. Rukhadz, E.G., Talyzenkova, G.P., and Terentev, A.P., *Zh. Obshch. Khim.*, 39(2), 401 (1969).
12. Fujii, Y., *Bull. Chem. Soc. Japan.*, 42(5), 1301 (1969).
13. Tamaki, M., *Bull. Chem. Soc., Japan.*, 45(5), 1400 (1972).
14. Biedermann, H.G., *Z. Naturforsch. B.*, 27(11), 1329 (1972).
15. Kasahara, A., *Bull. Chem. Soc. Japan.*, 41(9), 2185 (1968).
16. Sen, D.N., *Ind. J. Chem.*, 4(10), 454 (1966).
17. Singh, P.R., and Sahai, R., *J. Ind. Chem. Soc.*, 49(3), 211 (1972).
18. Nonhebel, D.C., *J. Chem. Soc.*, 4628 (1962).
19. Patil, J.N., and Sen, D.N., *Ind. J. Chem.*, 12(2), 189 (1974).
20. Lindoy, L.F., Hyascinth, C.L., and Wayne, E.M., *J. Chem. Soc., (Dalton)* 45 (1974).
21. Thaker, B.T., and Bhattacharya, P.K., *Bull. Chem. Soc. Japan*, (in press).

22. Collman, J.P., Matshall, R.L., Young, W.L., and Goldby, S.D.,
Inorg.Chem., 1, 704 (1962).
23. Bachman, G.B., and Dever, J.L., J.Am.Chem.Soc., 80, 5871
(1958).
24. Gluvchinsky, P., and Mockler, G.M., J.Chem.Soc., (Dalton)
1156 (1974).