July, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *1979—1983(1993)*

Syntheses and Spectral Properties of Dinitrosylmolybdenum(0) and Dioxomolybdenum(VI) Complexes

Mannar R. Maurya* and Changaramponnath Gopinathan
Inorganic Chemistry Division, National Chemical Laboratory, Pune 411008, India

(Received December 21, 1992)

Syntheses of dinitrosylmolybdenum(0) complexes of Schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, *o*-hydroxyacetophenone, and *p*-nitrobenzoylhydrazide have been carried out in one step by the reaction of [Mo(acac)$_2$(NO)$_2$] (acacH=acetylacetone) and the Schiff bases. The complexes are of the type [Mo(LH)$_2$(NO)$_2$] (LH$_2$=Schiff base) in which Schiff bases behave as monobasic bidentate ligands and coordinate to molybdenum through the azomethine nitrogen and enolic oxygen of the hydrazide moiety after deprotonation. Two geometrical isomers with nitrosyl groups trans to each other have been noticed in solution. Dioxomolybdenum(VI) complexes of the above Schiff bases have also been synthesized using [MoO$_2$(acac)$_2$] as precursor for comparison.

Dinitrosylmolybdenum(0) complexes have received considerable attention due to their use as a catalyst precursor or homogeneous catalyst as such.[1—4] Most of the reported dinitrosyl molybdenum complexes are restricted to either halogen or η-cyclopentadienyl. Only limited reports are available in the literature where classical ligands are coordinated to the molybdenum in addition to the nitrosyl[5] and only one report dealing with the synthesis of dinitrosylmolybdenum(0) complexes of Schiff bases has been reported recently.[6] This is mainly due to nonavailability of a suitable precursor. In our recent communication[6] we have reported [Mo(acac)$_2$(NO)$_2$] as a starting material for the first time and have shown that dinitrosylmolybdenum(0) complexes of the Schiff bases can be prepared by ligand exchange process, i.e., exchange of acetylacetone with Schiff bases, in a suitable solvent under aerobic conditions. Such ligand exchange reactions have been studied extensively in the case of dioxometal cations such as dioxomolybdenum(VI),[7] dioxotungsten(VI),[8] dioxouranium(VI)[9] etc. using [MO$_2$(acac)$_2$] (M=Mo, W or U) as the starting material. To establish the suitability of [Mo(acac)$_2$(NO)$_2$] as a precursor, we have now studied its reactivity towards the Schiff bases **A** and **B** (Fig. 1) and report that [Mo(acac)$_2$(NO)$_2$] can be readily used to prepare dinitrosylmolybdenum(0) complexes of these ligands in a single step process. We have also prepared dioxomolybdenum(VI) complexes of these ligands for comparison and spectral properties of the resulted complexes are reported here.

Experimental

Materials. The chemicals used were of analytical reagent grade. Acetylacetone, salicylaldehyde, and *o*-hydroxyacetophenone were distilled before use. The Schiff bases **A** and **B** were prepared following the literature procedure.[10] [Mo(acac)$_2$(NO)$_2$][11] and [MoO$_2$(acac)$_2$][12] were prepared by the methods described previously.

Synthesis of [Mo(LH)$_2$(NO)$_2$]. A solution of [Mo(acac)$_2$(NO)$_2$] (0.354 g, 1 mmol) in 5 cm^3 of methanol was added to a hot solution of the appropriate Schiff base (2 mmol) in 50 cm^3 of methanol and the reaction mixture was refluxed on a water bath for 2 d (4 d in case of H$_2$hap-NO$_2$BZH). The separated solid was filtered while hot, washed with methanol and dried. Finally, the complexes were purified by suspending in 40 cm^3 of methanol and refluxing for 3 h.

Synthesis of [MoO$_2$L]. A mixture of [MoO$_2$(acac)$_2$] (0.33 g, 1 mmol) and appropriate Schiff base (1 mmol) in 15 cm^3 of methanol was refluxed on a water bath for 5 h. The complex [MoO$_2$(sal-NO$_2$BZH)] precipitated during refluxing. After keeping the reaction mixture over night at ambient temperature, the complexes separated were filtered, washed with methanol, dried and finally recrystallized from methanol.

The complexes were dried at 130 °C to constant weight. Their analytical and physicochemical data are collected in Table 1.

Measurements. Molybdenum content was estimated gravimetrically as dioxobis(8-quinolinolato)molybdenum(VI) after decomposing the complexes with few drops of concd HNO$_3$ and H$_2$SO$_4$ and then igniting in a muffle furnace at ca. 450 °C. Other elemental analyses were performed by the microanalytical section of this laboratory. IR spectra were recorded in KBr on a Perkin–Elmer model 1620 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on Bruker WH-200 spectrometer in DMSO-d_6. The elec-

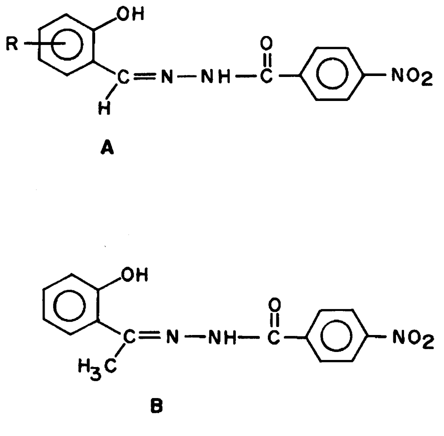


Fig. 1. Structure of the Ligands. (**A**) R=H, (H$_2$sal-NO$_2$BZH); R=5-Cl, (H$_2$clsal-NO$_2$BZH), (**B**) (H$_2$hap-NO$_2$BZH)

Table 1. Analytical and Physicochemical Data of the Complexes [a)]

Compound Stoichiomety	Yield %	Color	Found (Calcd) C	 H	 N	 Mo	Λ_M [b)]
[Mo(Hsal-NO$_2$BZH)$_2$(NO)$_2$] $C_{28}H_{20}N_8O_{10}Mo$	65	Orange yellow	46.10 (46.42)	2.71 (2.78)	15.32 (15.47)	13.16 (13.26)	2.5
[Mo(Hclsal-NO$_2$BZH)$_2$(NO)$_2$] $C_{28}H_{18}N_8O_{10}Cl_2Mo$	60	Orange yellow	42.52 (42.39)	2.25 (2.29)	13.94 (14.12)	12.33 (12.09)	3.0
[Mo(Hhap-NO$_2$BZH)$_2$(NO)$_2$] $C_{30}H_{24}N_8O_{10}Mo$	40	Dark brown	47.58 (47.88)	3.36 (3.21)	14.61 (14.89)	11.92 (12.75)	3.6
[MoO$_2$(sal-NO$_2$BZH)] $C_{14}H_9N_3O_6Mo$	65	Brown	40.56 (40.89)	2.19 (2.21)	10.41 (10.22)	23.00 (23.33)	4.5
[MoO$_2$(clsal-NO$_2$BZH)] $C_{14}H_8N_3O_6ClMo$	71	Orange	37.62 (37.73)	1.98 (1.81)	9.75 (9.43)	21.33 (21.53)	8.0
[MoO$_2$(hap-NO$_2$BZH)] $C_{15}H_{11}N_3O_6Mo$	66	Brownish yellow	42.08 (42.37)	2.59 (2.61)	9.67 (9.88)	22.82 (22.56)	7.4

a) Abbreviations: As under Fig. 1. b) Conductance values are in Ω^{-1} cm^2 mol^{-1}.

trical conductance measurements were done in 1×10^{-3} M DMF solution (1 M=1 mol dm^{-3}) using a Toshniwal conductivity bridge (Type CL01-02A) and a dip type cell calibrated with KCl solutions.

Results

The use of [Mo(acac)$_2$(NO)$_2$] as a starting material for dinitrosylmolybdenum(0) complexes was not known until we first reported it. We found that this precursor is very useful in preparing such complexes of the Schiff bases. Thus [Mo(acac)$_2$(NO)$_2$] undergoes ligand exchange reaction with the Schiff bases **A** and **B** in refluxing methanol to yield corresponding dinitrosyl complexes (Eq. 1).

$$[\mathrm{Mo(acac)_2(NO)_2}] + 2\mathrm{LH_2} \xrightarrow[\mathrm{MeOH}]{} [\mathrm{Mo(LH)_2(NO)_2}] + 2\mathrm{acacH}. \qquad (1)$$

It is interesting to note that only complexes of the composition [Mo(LH)$_2$(NO)$_2$] are formed under the reaction conditions, although we have also tried this reaction with other molar ratios. On the other hand, formation of the dioxomolybdenum(VI) complexes proceeded via Eq. 2

$$[\mathrm{MoO_2(acac)_2}] + \mathrm{LH_2} \xrightarrow[\mathrm{MeOH}]{} [\mathrm{MoO_2L}] + 2\mathrm{acacH}. \qquad (2)$$

and complexes of the composition [MoO$_2$L] are formed. Analytical data support complete removal of the coordinated acetylacetone in both cases and confirm the above compositions of the complexes.

The dinitrosyl complexes are insoluble in common solvents but soluble in coordinating solvents like DMF and DMSO whereas dioxo complexes are soluble in most of the solvents. The low molar conductance values 2.5—8.0 Ω^{-1} cm^2 mol^{-1} of the complexes in DMF indicate nonelectrolytic behavior of the complexes. The molecular weight measurements on the dinitrosylmolybdenum(0) complexes were not possible cryoscopically or ebulliometrically due to insolubility of the complexes in suitable organic solvents. However, in the light of known X-ray crystal structure of the monomeric complex, [Mo(pic)$_2$(NO)$_2$] (Hpic=2-pyridinecarboxylic acid),[13] we suggest a monomeric nature for the dinitrosyl complexes reported here. The [MoO$_2$L] type complexes are suggested to have oligomeric structure (vide infra).

^{1}H NMR Studies. The ^{1}H NMR spectra of the H$_2$clsal-NO$_2$BZH and its dinitrosylmolybdenum(0) and dioxomolybdenum(VI) complexes are reproduced in Fig. 2. Table 2 summarizes the NMR spectral data of

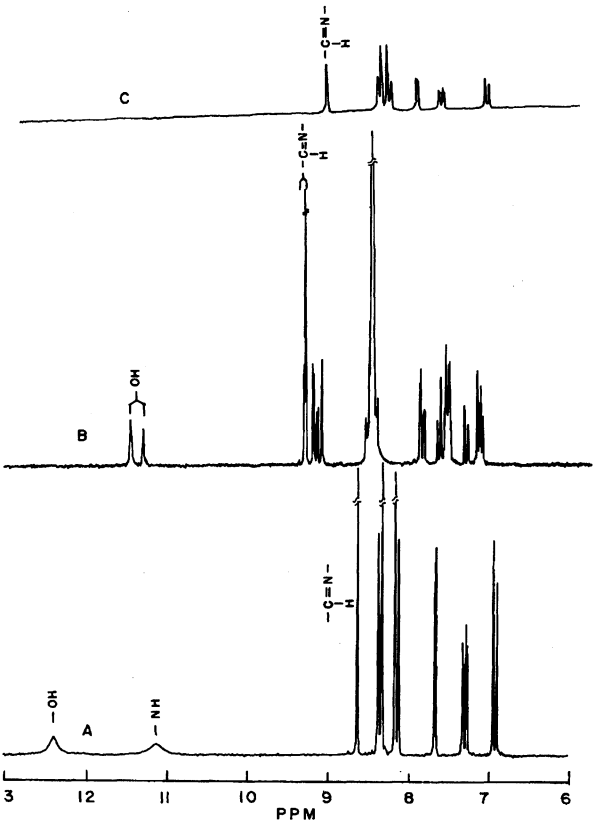


Fig. 2. ^{1}H NMR spectra. (A) H$_2$clsal-NO$_2$BZH, (B) [Mo(Hclsal-NO$_2$BZH)$_2$(NO)$_2$], and (C) [MoO$_2$(clsal-NO$_2$BZH)].

Table 2. ^{1}H NMR Spectral Data (δ in ppm) of the Ligands and Their Complexes [a)]

Compound	$-\underset{\mid}{C}=N-$ H	Aromatic protons	-NH-	-OH
H_2sal-NO_2BZH	8.68 (s)	6.90—8.44 (m)	11.10 (s)	12.38 (s)
[Mo(Hsal-NO_2BZH)$_2$(NO)$_2$]	9.22 (s), 9.24 (s)	7.00—9.40 (m)		11.14 (s), 11.24 (s)
H_2clsal-NO_2BZH	8.64 (s)	6.92—8.39 (m)	11.12 (s)	12.40 (s)
[Mo(Hclsal-NO_2BZH)$_2$(NO)$_2$]	9.28 (s), 9.29 (s)	7.05—9.18 (m)		11.27 (s), 11.45 (s)
H_2hap-NO_2BZH	2.50 (s) [b)]	6.91—8.41 (m)	11.65 (s)	13.25 (s)
[MoHhap-NO_2BZH)$_2$(NO)$_2$]	2.97 (s), 3.00 (s) [b)]	6.93—8.35 (m)		12.92 (s), 12.94 (s)
[MoO_2(sal-NO_2BZH)]	9.02 (s)	6.95—8.40 (m)		
[MoO_2(clsal-NO_2BZH)]	9.0 (s)	6.95—8.45 (m)		
[MoO_2(hap-NO_2BZH)]	2.92 (s) [b)]	6.92—8.38 (m)		

a) Letters given in parentheses indicate the type of signal. s=singlet, m=multiplet. b) Methyl protons signal of *o*-hydroxyacetophenone residue.

the ligands and their complexes. The Schiff bases **A** exhibit the azomethine proton resonance at δ=8.64—8.68 as a sharp singlet. In the spectra of the dinitrosyl complexes, this signal shifts to down field and splits into two signals. The downfield shift suggests the coordination of the azomethine nitrogen to molybdenum[14)] while splitting of the signal may be due to the presence of two isomeric forms in solution as discussed later. Similarly methyl protons of the Schiff base H_2hap-NO_2BZH resonate at δ=2.50 as singlet and shifts to downfield with splitting on complexation. The Schiff bases also exhibit two broad singlets at δ=11.10—11.65 and 12.38—13.25 due to NH and hydrogen bonded phenolic protons, respectively. The disappearance of NH proton signal in the complexes indicates the enolization of the keto group and subsequent coordination of the deprotonated enolic oxygen. Further, the two resonances due to the phenolic protons are observed at δ=11.14—12.92 and 11.24—12.94 which suggest the existence of free phenolic group in the nitrosyl complexes. A slightly upfield shift of the phenolic OH resonances in the complexes is expected due to breaking of the hydrogen bond between the phenolic hydrogen and azomethine nitrogen atoms. Thus the Schiff bases behave as monobasic bidentate moieties in dinitrosyl complexes coordinating through the azomethine nitrogen and enolic oxygen. Absence of both phenolic and NH proton resonances and downfield shift of the azomethine proton resonance (methyl protons resonance in the case of H_2hap-NO_2BZH) in the dioxomolybdenum(VI) complexes commensurate with the dibasic tridentate behavior of the ligands in these complexes. The resonances due to aromatic protons become little more complex and widely spaced in dinitrosyl complexes whereas in dioxo complexes they remain almost unchanged.

IR Studies. A partial listing of IR spectral data of the ligands and their complexes is given in Table 3. The Schiff bases exhibit two bands in the regions 3208—3306 and 1650—1665 cm^{-1}. These bands disappear in the complexes indicating the destruction of the carbonyl moiety due to enolization and consequent proton replacement with molybdenum, further supported by the appearance of a new band at 1230—1278 cm^{-1} due to the ν(C–O) (enolic) stretch.[15)] A strong band in the region 1603—1619 cm^{-1} is assigned to the ν(C=N) (azomethine) stretch and this band undergoes a negative shift of 5—13 cm^{-1} in the complexes thereby indicating the participation of the azomethine nitrogen atom in coordination.[16)] The ν(N–N) band appearing at 967—977 cm^{-1} in the ligands shifts to higher frequency by 37—46 cm^{-1} upon complexation. The magnitude of this shift indicates the monodentate coordination of $>$N–N$<$ residue as shift of $>$ 50 cm^{-1} is usually observed in bidentate coordination.[17)] A shift to the higher frequency is expected due to reduction

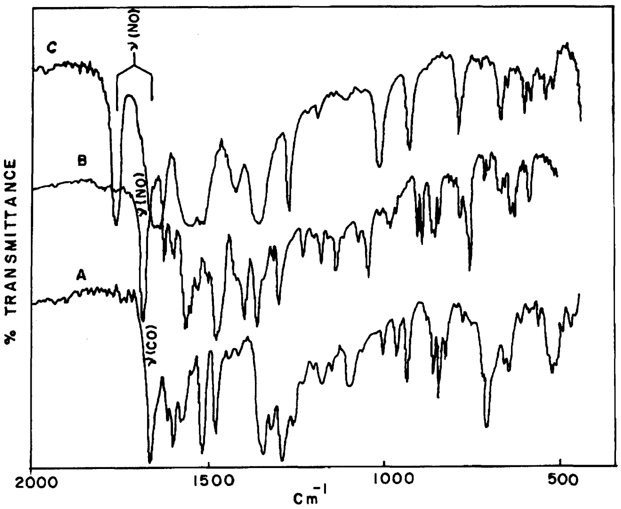


Fig. 3. IR spectra in the region 2000—500 cm^{-1}. (A) H_2clsal-NO_2BZH, (B) [Mo(Hclsal-NO_2BZH)$_2$(NO)$_2$], and (C) [Mo(acac)$_2$(NO)$_2$].

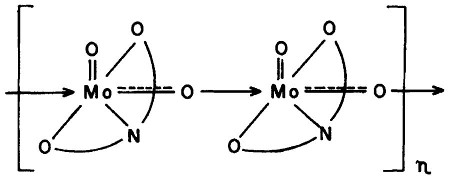
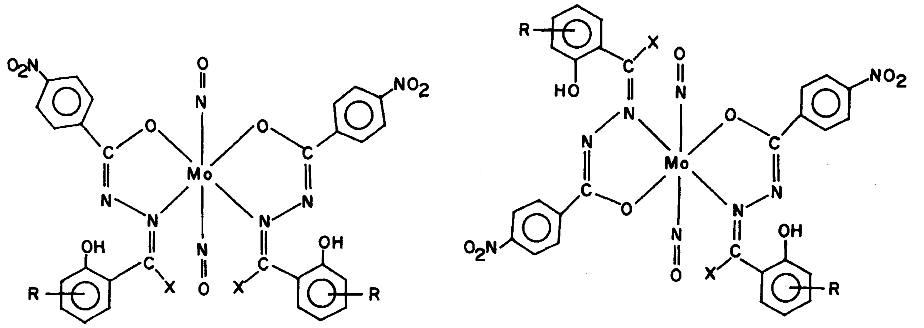


Fig. 4. Oligomeric structure of [MoO_2L].

Table 3. IR spectral Data (in cm^{-1}) of the Ligands and their Complexes

Compound	ν (C=O)	ν (NO)	ν (O=Mo=O)	ν (C=N)	ν (C–O) (enolic)	ν (N–N)
H_2sal-NO_2BZH	1650			1619		967
Ho(Hsal-NO_2BZH)$_2$(NO)$_2$]		1666		1612	1278	1013
H_2clsal-NO_2BZH	1665			1619		972
[Mo(Hclsal-NO_2BZH)$_2$(NO)$_2$]		1677		1614	1278	1012
H_2hap-NO_2BZH	1665			1603		977
[Mo(Hhap-NO_2BZH)$_2$(NO)$_2$]		1666		1598	1242	1014
[MoO_2(sal-NO_2BZH)]			947	1609	1238	1010
[MoO_2(clsal-NO_2BZH)]			946	1612	1263	1007
[MoO_2(hap-NO_2BZH)]			941	1590	1230	1012



C **D**

Fig. 5. Proposed structure for [Mo(LH)$_2$(NO)$_2$].

of the lone pair–lone pair repulsive forces of the adjacent nitrogen atoms.[18] The Schiff bases exhibit a broad band at 2800—3000 cm^{-1} which is assigned to the intramolecularly hydrogen bonded (OH) stretch. Absence of this band and appearance of a new band at ca. 3400 cm^{-1} only in the dinitrosyl complexes suggest the existence of free phenolic group in them. Thus the Schiff bases behave as a dibasic tridentate ligands in dioxomolybdenum(VI) complexes while as monobasic bidentate moieties in dinitrosylmolybdenum(0) complexes. Similar tridentate behavior of the Schiff bases in [MO_2L] (M = Mo, W; LH_2 = dibasic tridentate Schiff base)[8,19] and bidentate behavior of the Schiff base in [UO_2(Hsal-BZH)$_2$] (H_2sal-BZH=Schiff base derived from salicylaldehyde and benzoylhydrazide)[10] have been confirmed.

IR spectra of the dinitrosyl complexes also show distinct changes in the ν (NO) band positions relative to those of [Mo(acac)$_2$(NO)$_2$] which shows two strong bands at 1763 and 1654 cm^{-1} due to ν(NO) stretches of *cis*-Mo(NO)$_2$ moiety (Fig. 3).[11] In the nitrosyl complexes reported here, IR spectra show only one band centred at 1666—1677 cm^{-1} indicating a trans disposition of the NO group. Although these spectral changes are also consistent with a mononitrosyl complex, the analytical data suggest the presence of two nitrosyl group. The [MoO_2L] exhibit one ν(Mo=O) stretch at 941—947 cm^{-1} and a strong, broad band at 837—850 cm^{-1} due to the $\cdots$Mo=O$\rightarrow$Mo=O$\cdots$ interaction.[20] The data suggest the presence of an oligomeric structure for [MoO_2L].[19] In the oligomeric structure each molybdenum ion achieves a pseudooctahedral structure as shown in Fig. 4 via oxo bridging.

Discussion

The growth of dinitrosylmolybdenum(0) chemistry is limited due to nonavailability of the right starting material. By using [Mo(acac)$_2$(NO)$_2$] as a precursor, we have devised a general method for the synthesis of the Schiff base complexes of dinitrosylmolybdenum(0). Although reactivity of [Mo(acac)$_2$(NO)$_2$] towards the Schiff bases, in general, seems to be rather low in comparison to that of [MoO_2(acac)$_2$], this process is advantageous over the old ones as this can be used in aerobic conditions. It is also interesting to note that during the exchange reaction nitrosyl groups remain intact and do not oxidize to oxo species; these nitrosyl complexes do not furnish any IR band in the O=Mo=O stretching frequency region. Further, presence of only one band at ca. 1670 cm^{-1} due to ν(NO) stretch strongly support the isomerization of the nitrosyl groups from cis in the precursor, [Mo(acac)$_2$(NO)$_2$] to trans in the Schiff base complexes during reaction; the *cis*-Mo(NO)$_2$ structure would show two bands in the region ca. 1700 cm^{-1}.

On the basis of the *trans*-dinitrosyl geometry, the complexes are expected to show two geometrical isomers **C** and **D** (Fig. 5) and both the isomers are expected to show only one signal each for the phenolic and azomethine protons in the ^{1}H NMR spectra. However, chemical shift should be different due to different arrangements of the ligands around the molybdenum ion. The NMR spectra indeed show two sets of signals for each proton indicating the presence of both isomers in solution. Unfortunately it is not possible to distinguish between the set of the signals for the each particular isomer at the moment. However, on the basis of the area integration ratios the percentage of these isomers in solution is approximated to be 60:40. We are also unable to separate these isomers due to insolubility of the complexes in common solvents.

M.R.M. is thankful to the Council of Scientific and Industrial Research, New Delhi 110012 for the award of Pool Officership.

References

1) A. Keller, *J. Mol. Catal.*, **53**, L9 (1989).
2) A. Keller, *Inorg. Chim. Acta*, **149**, 165 (1988).
3) E. A. Zuech, *J. Chem. Soc., Chem. Commun.*, **1968**, 1182.
4) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and T. Kittleman, *J. Am. Chem. Soc.*, **92**, 528 (1970).
5) M. Minelli, J. L. Hubbard, and J. H. Enemark, *Inorg. Chem.*, **23**, 970 (1984).
6) M. R. Maurya, S. Gopinathan, C. Gopinathan, and R. C. Maurya, *Polyhedron*, **12**, 159 (1993).
7) A. Syamal and M. R. Maurya, *Coord. Chem. Rev.*, **95**, 183 (1989).
8) S. -B. Yu and R. H. Holm, *Inorg. Chem.*, **28**, 4385 (1989).
9) R. L. Dutta and A. K. Pal, *Indian J. Chem., Sect. A*, **24**, 76 (1985).
10) A. Syamal and B. K. Gupta, *Rev. Roum. Chim.*, **26**, 857 (1981).
11) S. Sarkar and P. Subramanian, *Inorg. Chim. Acta*, **35**, L357 (1979).
12) G. J. -J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).
13) M. F. Perpinan, L. Ballester, A. Stones, A. Monge, C. Ruiz-Valero, and E. G. Puebla, *Polyhedron*, **6**, 1523 (1987).
14) E. C. Alyea, A. Malek, and A. I. Kazi, *Transition Met. Chem.*, **6**, 233 (1981).
15) a) A. Syamal and K. S. Kale, *Indian J. Chem., Sect. A*, **19**, 225 (1980); b) A. Syamal and M. R. Maurya, *Transition Met. Chem., (Weinheim. Ger.)*, **11**, 205 (1986).
16) P. Teyssie and J. J. Charette, *Spectrochim. Acta*, **19**, 1407 (1963).
17) A. Braibanti, F. Dallvalle, M. A. Pellinghellli, and E. Laporati, *Inorg. Chem.*, **7**, 1430 (1968).
18) S. P. Perlepes, D. Nicholls, and M. R. Harrison, *Inorg. Chim. Acta*, **102**, 137 (1985).
19) a) O. A. Rajan and A. Chakrvorty, *Inorg. Chem.*, **20**, 660 (1981); b) A. Syamal and M. R. Maurya, *Synth. React. Inorg. Met. -Org. Chem.*, **16**, 857 (1986); c) A. Syamal and M. R. Maurya, *Indian J. Chem., Sect. A*, **25**, 934 (1986).
20) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).