Bull. Chem. Soc. Jpn., ***68***, *554—558(1995)*

Binuclear Dioxomolybdenum(VI) Complexes of Flexibly-Bridged Hexadentate Tetraanionic Schiff's Bases Derived from Methylene- or Dithio-bis(salicylaldehyde) and *S*-Methyldithiocarbazate or *S*-Benzyldithiocarbazate

Mannar R. Maurya,* Deena C. Antony,† Sarada Gopinathan,† and Changaramponnath Gopinathan*,†

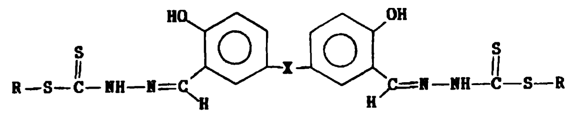
Department of Chemistry, University of Poona, Pune 411007, India

†Inorganic Chemistry Division, National Chemical Laboratory, Pune 411008, India

(Received May 26, 1994)

The flexibly-bridged hexadentate tetraanionic ligands, LH_4 [LH_4=Schiff's bases obtained by the condensation of methylene- or dithio-bis(salicylaldehyde) with *S*-methyldithiocarbazate and *S*-benzyldithiocarbazate], react with $[MoO_2(acac)_2]$ in a 1:2 molar ratio in refluxing methanol to give complexes of the type $[(MoO_2)_2L]$. These complexes show an intense ν(Mo=O) band at 924—948 cm^{-1} and a broad but strong band at ca. 850 cm^{-1} due to weakened ν(Mo=O) as a result of Mo$\overset{--}{=}$O→Mo interactions. An oligomeric structure, in which each Mo(VI) ion achieves a pseudo-octahedral structure via Mo$\overset{--}{=}$O→Mo bridging, has been suggested for these complexes. $[(MoO_2)_2L]$ reacts with monodentate ligands (D) like pyridine, 4-methylpyridine, and dimethylsulfoxide and forms six-coordinated complexes of the type $[(MoO_2)_2L(D)_2]$ which are monomers. Cyclic voltammetry measurements indicate that these $Mo^{VI}O_2$ complexes are resistant to $Mo^{IV}O$ reduction.

The coordination complexes of molybdenum in higher oxidation states are generally associated with an oxo-group.[1—3] The oxomolybdenum unit (Mo=O or $\overset{\overset{O}{\|}}{Mo}$=O) was shown to be present in various enzymes.[4] In these enzymes, molybdenum cycles between the +VI and +IV oxidation states by a reversible oxo-transfer reaction.[5,6] Although the chemistry of mononuclear $Mo^{VI}O_2$ Schiff's base complexes has been extensively investigated and is well understood,[3] binuclear $Mo^{VI}O_2$ complexes have only recently been reported by us.[7,8] The binuclear $Mo^{VI}O_2$ complexes of flexibly-bridged hexadentate tetraanionic (ONO⌒ONO donor) Schiff's base ligands are oligomers in which each Mo(VI) ion achieves a pseudo-octahedral structure via oxo bridging. Cyclic voltammetry measurements show irreversible to quasireversible reduction of the $Mo^{VI}O_2$ complexes to the $Mo^{IV}O$ species, with a cathodic reduction potential of −0.83 to −0.85 V vs. SCE at a scan rate of 200 mV s^{-1}. We now report the binuclear $Mo^{VI}O_2$ complexes of new flexibly-bridged hexadentate tetraanionic (SNO⌒ONS donor) Schiff's base ligands (**A**) (Chart 1). The spectral and electrochemical properties of the isolated complexes are presented here.



(**A**)

	X	R	Abbreviations
1	CH_2	CH_3	$CH_2(H_2sal\text{-}SMDTC)_2$
2	CH_2	$CH_2C_6H_5$	$CH_2(H_2sal\text{-}SBDTC)_2$
3	S–S	CH_3	$S_2(H_2sal\text{-}SMDTC)_2$
4	S–S	$CH_2C_6H_5$	$S_2(H_2sal\text{-}SBDTC)_2$

Chart 1.

Experimental

Materials. Ammonium molybdate(VI) tetrahydrate, salicylaldehyde, and acetylacetone were procured from standard sources and were of analytical reagent grade. Acetylacetone and salicylaldehyde were distilled before use. *S*-Methyldithiocarbazate,[9] *S*-benzyldithiocarbazate,[10] methylenebis(salicylaldehyde),[11] dithiobis(salicylaldehyde),[12] and $[MoO_2(acac)_2]$[13] (acacH=acetylacetone) were prepared by the literature methods.

Preparation of the Schiff's Bases. A hot methanolic solution (ca. 10 cm^3) of methylenebis(salicylaldehyde) (0.256 g, 1 mmol) or dithiobis(salicylaldehyde) (0.306 g, 1 mmol) was added to a hot solution of the respective dithiocarbazate (2 mmol) in 10 cm^3 of methanol and the reaction mixture was refluxed for 3 h on a water bath. After reducing the solvent to ca. 10 cm^3, the solution was cooled to 10 °C overnight. The separated solid was filtered, washed with methanol, dried at ambient temperature, and finally recrystallized from hot methanol; yield: 70—80%.

Preparation of the Complexes. **$[(\mathrm{MoO_2})_2(\mathrm{CH_2}\{\text{sal-SMDTC}\}_2)]$.** To a hot solution of the ligand $\mathrm{CH_2(H_2sal\text{-}SMDTC)_2}$ (0.464 g, 1 mmol) in methanol (40 $\mathrm{cm^3}$), $[\mathrm{MoO_2(acac)_2}]$ (0.66 g, 2 mmol) was added with vigorous shaking. The resulting turbid solution was filtered and then refluxed on a water bath for 6 h. After reducing the volume of the solution to ca. 10 $\mathrm{cm^3}$, it was cooled to 10 °C overnight. The separated solid was filtered, washed with methanol, and dried in air at 100 °C; yield: 70%.

Other complexes listed in Table 1 were prepared following the above method, or with slight variations thereof, in 70—80% yields.

$[(\mathrm{MoO_2})_2(\mathrm{CH_2}\{\text{sal-SMDTC}\}_2)(\mathrm{D})_2]$ (D=DMSO, py, pic).[14] $[(\mathrm{MoO_2})_2(\mathrm{CH_2}\{\text{sal-SMDTC}\}_2)]$ (0.20 g) was dissolved in a respective solvent (5 $\mathrm{cm^3}$) by heating on a water bath. Partial evaporation of the solvent to about 2 $\mathrm{cm^3}$ under vacuum produced a solid compound which was filtered, washed with ether, and dried under vacuum; yield: 80%.

The analytical and other physicochemical data for the new Schiff's bases and their $\mathrm{Mo^{VI}O_2}$ complexes are presented in Table 1.

Measurements. Elemental analyses of the ligands and complexes were carried out at the microanalytical section of the National Chemical Laboratory. Details of other techniques were reported in our previous papers.[7,8]

Results and Discussion

A freshly-prepared solution of the methylene- and dithiobis(salicylaldehyde) reacted with *S*-methyldithiocarbazate or *S*-benzyldithiocarbazate in a 1 : 2 molar ratio to give flexibly-bridged hexadentate tetraanionic Schiff's bases **1**, **2**, **3**, and **4**. While the elemental and physicochemical data suggested the formation of the Schiff's bases, the spectral data (vide infra) confirmed the existence of these in their thione form as shown by structure (**A**).

The reaction of the flexibly-bridged ligands with $[\mathrm{MoO_2(acac)_2}]$ in a 1 : 2 molar ratio proceeded as follows [Eq. 1] in refluxing methanol and complexes of the type $[(\mathrm{MoO_2})_2\mathrm{L}]$ were formed.

$$2\,[\mathrm{MoO_2(acac)_2}] + \mathrm{LH_4} \xrightarrow[\mathrm{MeOH}]{} [(\mathrm{MoO_2})_2\mathrm{L}] + 4\,\mathrm{acacH} \quad (1)$$

The analytical data support the formation of the complexes by complete removal of the coordinated acetylacetone group under the present reaction conditions. These complexes do not undergo any weight loss on heating up to 200 °C which suggests the formation of the five-coordinated complex $[(\mathrm{MoO_2})_2\mathrm{L}]$ and not the expected octahedral complex $[(\mathrm{MoO_2})_2\mathrm{L{\cdot}2MeOH}]$. Weakly-coordinated monodentate ligands like methanol in complexes of the type $[\mathrm{MoO_2L{\cdot}MeOH}]$ are known to undergo cleavage even at room temperature.[3] However, strong coordinating ligands (D) like DMSO, pyridine, and 4-methylpyridine do form octahedral complexes, $[(\mathrm{MoO_2})_2\mathrm{L(D)_2}]$ when the complexes are dissolved in them. All the complexes are non-electrolytes (4.4—5.5 $\Omega^{-1}\,\mathrm{mol^{-1}\,cm^2}$) in DMF and are diamagnetic as expected for the 4d° system. They are soluble in coordinating solvents such as DMSO, DMF, THF, and pyridine. The high decomposition temperature (>250 °C) of the complexes indicates their increased thermal stability.

IR and Electronic Spectral Studies. A partial listing of the IR spectral data of the ligands and $\mathrm{Mo^{VI}O_2}$ complexes is given in Table 2. The Schiff's bases exhibit a strong band at 1030—1052 $\mathrm{cm^{-1}}$ due to the ν(C=S) band which indicates the thione nature of the ligands.[15] This is further supported by the presence of a band in the region 3095—3248 $\mathrm{cm^{-1}}$ due to the ν(NH) band of the hydrazide residue. The disappearance of bands due to ν(C=S) and ν(NH) in the spectra of the complexes supports the thioenolization of the >C=S group and coordination of the sulphur to molybdenum. A broad band around 3400 $\mathrm{cm^{-1}}$ is assigned to the ν(OH) (phenolic) band and the absence of this band in the complexes suggests the coordination of the phenolic oxygen atom. This is further supported by the shift of the ν(C–O) (phenolic) band from 1510—1539 $\mathrm{cm^{-1}}$ of the Schiff's bases to 1539—1552 $\mathrm{cm^{-1}}$ in the complexes. The ν(C=N) (azomethine) band of the ligands appears at 1607—1624 $\mathrm{cm^{-1}}$ and this band is shifted to a lower frequency by 16—18 $\mathrm{cm^{-1}}$ in the complexes, indicating coordination through the azomethine nitrogen atom.[16] Thus the IR data suggest that both the Schiff's base units attached to the $-\mathrm{CH_2}$ or –S–S– groups behave as dibasic tridentate ONS donor ligands. The coordination of the monodentate ligands in the adducts has also been confirmed by the presence of their characteristic vibrational mode(s).[17]

The $[(\mathrm{MoO_2})_2\mathrm{L}]$ complexes exhibit a sharp single band (two bands in **4a**) at 924—948 $\mathrm{cm^{-1}}$ due to the ν(O=Mo=O) stretch and a strong but broad band at ca. 850 $\mathrm{cm^{-1}}$ due to the $\mathrm{Mo{\cdots}O{\rightarrow}Mo}$ interaction.[1] However, in adducts $[(\mathrm{MoO_2})_2\mathrm{L(D)_2}]$ the 850 $\mathrm{cm^{-1}}$ band is uniformly absent and they show two characteristic IR bands at 950 and 920 $\mathrm{cm^{-1}}$ due to the ν_{sym} and ν_{asym} (O=Mo=O) modes of the *cis*-$\mathrm{MoO_2}$ structure. These observations suggest the presence of an oligomeric (pseudooctahedral) structure for $[(\mathrm{MoO_2})_2\mathrm{L}]$ in which each Mo(VI) ion achieves a pseudooctahedral structure through an oxygen bridge involving an oxygen of the $\mathrm{MoO_2}$ moiety. A probable oligomeric structure through $\mathrm{Mo{\cdots}O{\rightarrow}Mo}$ bridging is shown in Fig. 1. Adduct formation essentially accounts for the disappearance of the 850 $\mathrm{cm^{-1}}$ band due to breaking of the $\mathrm{Mo{\cdots}O{\rightarrow}Mo}$ bridge and the appearance of the doublet characteristic of the *cis*-$\mathrm{MoO_2}$ species. The observation of ν(C–O) (phenolic) at identical positions in **1a** and its adducts (e.g.$[(\mathrm{MoO_2})_2(\mathrm{CH_2}\{\text{sal-SMDTC}\}_2)]$, 1552; $[(\mathrm{MoO_2})_2(\mathrm{CH_2}\{\text{sal-SMDTC}\}_2)(\mathrm{DMSO})_2]$, 1551; $[(\mathrm{MoO_2})_2(\mathrm{CH_2}\{\text{sal-SMDTC}\}_2)(\mathrm{py})_2]$, 1552; $[(\mathrm{MoO_2})_2(\mathrm{CH_2}\{\text{sal-SMDTC}\}_2)(\mathrm{pic})_2]$, 1552 $\mathrm{cm^{-1}}$) further supports the presence of an oligomeric bridge

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

S. no.	Compound stoichiometry	Color	Mp °C	Found (Calcd)/% C	H	N	S
1	$CH_2(H_2sal\text{-}SMDTC)_2$	Yellow	222	49.49	4.68	12.21	27.81
	$C_{19}H_{20}N_4O_2S_4$			(49.11)	(4.34)	(12.06)	(27.60)
2	$CH_2(H_2sal\text{-}SBDTC)_2$	Pale	220	59.97	4.90	9.23	20.62
	$C_{31}H_{28}N_4O_2S_4$	yellow		(60.36)	(4.58)	(9.08)	(20.79)
3	$S_2(H_2sal\text{-}SMDTC)_2$	Yellow	226	42.26	3.82	10.62	37.15
	$C_{18}H_{18}N_4O_2S_6$			(42.00)	(3.52)	(10.88)	(37.38)
4	$S_2(H_2sal\text{-}SBDTC)_2$	Yellow	198	53.76	3.71	8.57	28.59
	$C_{30}H_{26}N_4O_2S_6$			(54.02)	(3.93)	(8.40)	(28.85)
1a	$[(MoO_2)_2(CH_2\{sal\text{-}SMDTC\}_2)]$	Brown	>250	31.81	1.97	7.53	17.61
	$C_{19}H_{16}N_4O_6S_4Mo_2$			(31.85)	(2.25)	(7.82)	(17.90)
2a	$[(MoO_2)_2(CH_2\{sal\text{-}SBDTC\}_2)]$	Orange	>250	42.45	2.84	6.23	14.93
	$C_{31}H_{24}N_4O_6S_4Mo_2$			(42.86)	(2.78)	(6.45)	(14.76)
3a	$[(MoO_2)_2(S_2\{sal\text{-}SMDTC\}_2)]$	Brown	>250	28.49	1.97	7.06	25.06
	$C_{18}H_{14}N_4O_6S_6Mo_2$			(28.20)	(1.84)	(7.31)	(25.10)
4a	$[(MoO_2)_2(S_2\{sal\text{-}SBDTC\}_2)]$	Orange	>250	39.03	2.29	6.01	21.10
	$C_{30}H_{22}N_4O_6S_6Mo_2$			(39.22)	(2.41)	(6.10)	(20.88)

a) Abbreviations: As under Structure **A**.

Table 2. IR and Electronic Spectral Data (cm^{-1})

Compounds	IR ν(C=S)	ν(C=N)	ν(O=Mo=O)	ν(Mo$\cdots$O$\rightarrow$Mo)	λ_{max} ($\log \varepsilon$)
1	1039	1623			38,000 (4.43), 30,864 (4.63), 27,932 (4.75)
1a		1605	924	816	37,735 (4.65), 31,153 (4.68), 24,449 (4.07)
2	1030	1624			38,022 (4.67), 33,444 (4.77), 30,769 (4.70), 26,455 (5.00)
2a		1606	948	853	37,735 (4.69), 31,055 (4.68), 24,691 (4.08)
3	1052	1608			37,878 (4.54), 30,674 (4.58), 27,472 (4.61)
3a		1592	931	888	37,735 (4.46), 34,965 (4.36), 24,691 (3.82)
4	1040	1607			38,168 (4.59), 33,557 (4.70), 25,706 (4.75)
4a		1591	947, 910	837	37,593 (4.86), 30,769 (4.76), 24,570 (4.18)

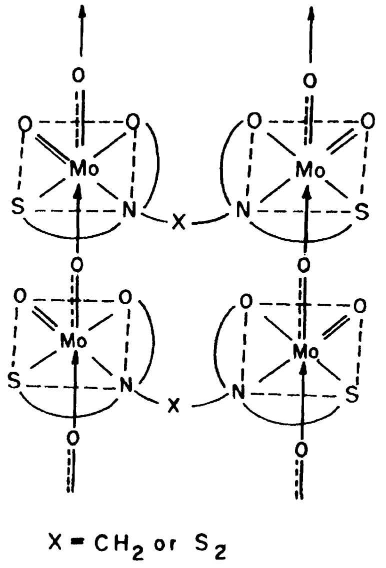


Fig. 1. Proposed oligomeric structure of $[(MoO_2)_2L]$.

via an oxygen of the MoO_2 group as oligomerization via phenolic oxygen bridging would show a significant change in the C–O stretch.[18)] Similar oligomeric structures for other $Mo^{VI}O_2$ and $W^{VI}O_2$ complexes having tridentate dibasic ONS and ONO donor ligands have been suggested.[3,19)]

The spectral data presented in Table 2 also show that all these Schiff's bases exhibit three or four electronic spectral bands. These bands are also observed in the complexes. In addition, a broad shoulder observed at around 24000 cm^{-1} is assigned to the ligand-to-metal charge transfer (lmct) band between the lowest empty d-orbital of molybdenum and the highest occupied ligand molecular orbital. The appearance of the lmct band as a shoulder with a relatively high extinction coefficient (see Table 2) is probably due to merging of the 25700—27472 cm^{-1} band of the free Schiff's bases with the lmct band in the complexes.

^{1}H NMR Studies. The ^{1}H NMR spectra of the Schiff's bases and the complexes were recorded in DMSO-d_6 and the chemical shifts (δ in ppm) are reported relative to DMSO-d_6 (2.40 ppm). The spectral data of the Schiff's bases and their complexes are summarized in Table 3. All the Schiff's bases exhibit a singlet at 10.05—10.65 ppm due to the –NH proton. The presence of –NH proton resonance and the absence

Table 3. ^{1}H NMR Spectral Data (δ in ppm)[a]

Compounds[b]	–CH=N–	Aromatic protons	–SCH$_2$	–CH$_2$–	–CH$_3$	–NH	–OH
1	8.45 (s, 2H)	6.75 (d, 2H), 7.13 (d, 2H), 7.45 (d, 2H)		3.80 (s, 2H)	2.47 (s, 6H)	10.05 (s, 2H)	13.30 (s, 2H)
1a	8.95 (s, 2H)	6.93 (d, 2H), 7.45 (d, 2H), 7.70 (d, 2H)		3.95 (s, 2H)	2.55 (s, 6H)		
2	8.50 (s, 2H)	6.80 (d, 2H), 7.50 (d, 2H), 7.35 (m, 12H)	4.50 (s, 4H)	3.75 (s, 2H)		10.10 (s, 2H)	13.35 (s, 2H)
2a	8.95 (s, 2H)	6.92 (d, 2H), 7.30 (m, 6H), 7.45 (d, 6H), 7.70 (d, 2H)	4.40 (s, 4H)	3.80 (s, 2H)			
3	8.45 (s, 2H)	6.88 (d, 2H), 7.42 (d, 2H), 7.85 (d, 2H)			2.50 (s, 6H)	10.60 (s, 2H)	13.27 (s, 2H)
3a	8.95 (s, 2H)	7.00 (d, 2H), 7.70 (d, 2H), 8.00 (d, 2H)			2.65 (s, 6H)		
4	8.47 (s, 2H)	6.88 (d, 4H), 7.32 (m, 10H), 7.77 (d, 2H)	4.50 (s, 4H)			10.65 (s, 2H)	13.35 (s, 2H)
4a	9.05 (s, 2H)	7.00 (d, 2H), 7.28 (m, 6H), 7.45 (d, 4H), 7.68 (d, 2H), 8.05 (d, 2H)	4.45 (s, 4H)				

a) Letters given in parentheses indicate the type of signal. s=singlet, d=doublet, m=multiplet. b) For abbreviations see Table 1.

of –SH proton resonance further supports the conclusion drawn from the IR spectra, namely the thione nature of the ligand. Usually –SH proton resonance is observed when such ligands exist in their tautomeric thiolo forms. The disappearance of the signal due to the –NH proton in the spectra of the complexes suggests the involvement of the –NH proton in the thioenolization of the >C=S group and subsequent coordination of the sulphur atom after proton replacement. The signal due to the phenolic proton, appearing at 13.27—13.35 ppm in the free Schiff's bases, is also absent on coordination and this indicates the deprotonation of the phenolic proton as a result of complex formation. The sharp singlet at 8.45—8.50 ppm due to the azomethine proton shifts downfield, indicating the coordination of the lone pair of electrons of the azomethine nitrogen.[20] The coordination of pyridine and 4-methyl pyridine to the molybdenum in the adducts is evidenced by the appearance of two or three new signals in the aromatic region. In addition, the methyl protons of 4-methylpyridine resonate at 2.30 ppm in $[(MoO_2)_2(CH_2\{sal\text{-}SMDTC\}_2)(pic)_2]$. Other resonances due to –CH$_2$– protons, –SCH$_2$– protons, –SCH$_3$ protons, and aromatic protons in the complexes appear in almost the same positions as in the respective Schiff's bases. The presence of a singlet at 3.75—3.95 ppm due to –CH$_2$– protons attached to two benzene rings in the Schiff's bases $CH_2(H_2sal\text{-}SMDTC)_2$ and $CH_2(H_2sal\text{-}SBDTC)_2$ and their complexes indicates that the two dibasic tridentate Schiff's base units are still attached to the methylene group.

Electrochemical Study. Cyclic voltammetry measurements of all the complexes were carried out at different temperatures (25—50 °C) and at various scan rates in DMF under dry nitrogen using 0.1 M tetrabutylammonium perchlorate (1 M=1 mol dm^{-3}) as a supporting electrolyte. However, no detectible reduction or oxidation waves were observed in any cyclic voltammogram. This is contrary to the observation reported for mononuclear Mo^{VI}O$_2$ complexes of very similar ONS donor ligands where all the complexes showed irreversible to quasireversible single electron reduction waves in their cyclic voltammograms.[21] The cyclic voltammograms of even Mo^{VI}O$_2$ complexes of flexibly-bridged ligands having an ONO$^\frown$ONO donor system showed irreversible to quasireversible reduction of the Mo(VI) to Mo(IV) species.[8]

The authors are thankful to Dr. K. Vijaya Mohanan for carrying out the cyclic voltammetry measurements. M.R.M. acknowledges the encouragement received from the Head of the Department of Chemistry.

References

1) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).

2) R. A. D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976).

3) A. Syamal and M. R. Maurya, *Coord. Chem. Rev.*, **95**, 183 (1989).

4) S. P. Cramer, H. B. Gray, and K. V. Rajagopalan, *J. Am. Chem. Soc.*, **101**, 2772 (1979); J. M. Berg, K. O. Hodgson, S. P. Cramer, J. L. Corbin, A. Elsberry, N. Pariyadath, and E. I. Stiefel, *J. Am. Chem. Soc.*, **101**, 2774 (1979); T. D. Tullius, D. M. Kurtz, Jr., S. D. Conradson, and K. O. Hodgson, *J. Am. Chem. Soc.*, **101**, 2776 (1979); S. P. Cramer, R. Wahl, and K. V. Rajagopalan, *J. Am. Chem. Soc.*, **103**, 7721 (1981).

5) R. C. Bray, *Enzymes*, **12**, 299 (1975); S. Gutteridge and R. C. Bray, "Chem. Uses Molybdenum Proc. Int. Conf., 3rd," Abstr., p. 275 (1979).

6) R. C. Bray in "Molybdenum Chemistry of Biological Significance," ed by W. E. Newton and S. Otsuka, Plenum

Press, New York (1980), p. 117.

7) M. R. Maurya, D. C. Antony, S. Gopinathan, and C. Gopinathan, *Polyhedron*, **12**, 2731 (1993).

8) M. R. Maurya, D. C. Antony, S. Gopinathan, C. Gopinathan, and K. V. Mohanan, *Indian J. Chem., Sect. A*, in press.

9) M. A. Ali, S. E. Livingstone, and D. J. Phillips, *Inorg. Chim. Acta*, **7**, 179 (1973).

10) M. A. Ali and M. T. H. Tarafder, *J. Inorg. Nucl. Chem.*, **39**, 1785 (1977).

11) C. S. Marvel and N. Tarkoy, *J. Am. Chem. Soc.*, **79**, 6000 (1957).

12) P. A. Awasarkar, S. Gopinathan, and C. Gopinathan, *Synth. React. Inorg. Met.-Org. Chem.*, **15**, 133 (1985).

13) G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).

14) These adducts were characterized by their IR and ^{1}H NMR spectra only.

15) M. A. Ali and R. Bose, *J. Inorg. Nucl. Chem.*, **39**, 265 (1977).

16) P. Teyssie and J. J. Charette, *Spectrochim. Acta*, **19**, 1407 (1963).

17) V. N. Krishnamurthy and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **29**, 517 (1967); S. S. Singh and C. B. S. Sengar, *Indian J. Chem.*, **7**, 812 (1969).

18) A. Syamal and K. S. Kale, *Inorg. Chem.*, **18**, 992 (1979).

19) A. Syamal and M. R. Maurya, *Indian J. Chem., Sect. A*, **25**, 934 (1986).

20) E. C. Alyea, A. Malek, and A. I. Kazi, *Transition Met. Chem. (Weinheim, Ger.)*, **6**, 223 (1981).

21) S. Bhattacharjee and R. G. Bhattacharyya, *J. Chem. Soc., Dalton Trans.*, **1992**, 1357; S. Bhattacharjee and R. G. Bhattacharyya, *J. Chem. Soc., Dalton Trans.*, **1993**, 1151.