

Available online at www.sciencedirect.com



Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 798 (2006) 89-101

www.elsevier.com/locate/molstruc

Metal nitrosyl complexes of bioinorganic, catalytic, and environmental relevance: A novel single-step synthesis of dinitrosylmolybdenum(0) complexes of {Mo(NO)₂}⁶ electron configuration involving Schiff bases derived from 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one and 4-aminoantipyrine, directly from molybdate(VI) and their characterization ☆

R.C. Maurya *, A. Pandey, J. Chaurasia, H. Martin

Coordination and Bioinorganic Chemistry Laboratory, Department of P.G. Studies and Research in Chemistry, R.D. University, Jabalpur 482 001, India

Received 17 October 2005; received in revised form 16 March 2006; accepted 20 March 2006 Available online 2 June 2006

Abstract

This paper reports the synthesis of five new hexa-coordinated mixed-ligand dinitrosyl complexes of molybdenum(0) of the composition [Mo(NO)₂(L)(OH)], where LH = N-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)-4-aminoantipyrine (mphvp-aapH), N-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-4-aminoantipyrine (bmphp-aapH), N-(3'-methyl-1'-phenyl-4'-propionylidene-2'-pyrazolin-5'-one)-4-aminoantipyrine (mphvp-aapH), N-(4'-acetylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-4-aminoantipyrine (amphp-aapH) or N-(-4'-iso-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-4-aminoantipyrine (amphp-aapH) or N-(-4'-iso-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-4-aminoantipyrine (iso-bumphp-aapH) directly from molybdate (VI) in a single step and in a single pot. The compounds so obtained have been characterized by elemental analyses, molar conductance, decomposition temperature and magnetic measurements, thermogravimetric analyses, infrared and electronic spectral studies. They were found to contain low-spin [Mo(NO)₂]⁶ electron configuration. A *cis*-octahedral structure has been proposed for these complexes. The 3D molecular modeling and analysis for bond lengths and bond angles have also been carried out for one of the representative compounds, [Mo(NO)₂(bmphp-aap)(OH)] (2).

© 2006 Published by Elsevier B.V.

Keywords: Dinitrosylmolybdenum(0) complexes; Pyrazolone based ligands; Bioinorganic; Catalytic; Environmental relevance; 3D molecular modeling

1. Introduction

The Schiff base derivatives [1] of 4-aminoantipyrine (4amino-2,3-dimethyl-1-phenyl-2-pyrazolin-5-one) received much attention due to their applications including biological, clinical, analytical and pharmacological areas. Even though 4-aminoantipyrine itself exhibits antimicrobial activity [2], it has reported to be enhanced due to the condensation with aldehydes, ketones, thiosemicarbazides, carbazides, etc.

The nitrosyl group's ability to bind to transition metals in a linear or a bent fashion [3–6], to behave as NO^+ or NO^- [6,7] and to influence, as well as be influenced by, other ligands in the coordination environment [8–20] has been of interest to coordination chemists and theoretical chemists for decades [21–23]. Catalytic applications [24–29] of transition metal nitrosyl complexes

^{*} Enemark and Feltham have proposed circumventing the problem of the nature of the nitrosyl ligand by considering metal nitrosyls as containing an $\{M(NO)_x\}^n$ group, where *n* is the number of electrons of M, plus the number of electrons in π^* -orbital of NO (or more conveniently, *n* is the number of d-electrons if nitrosyl is regarded as being coordinated as NO⁺). See Ref. [3].

^{*} Corresponding author. Fax: +91 761 2392120.

E-mail addresses: rcmauryajb@dataone.in, rcmaurya@sancharnet.in (R.C. Maurya).

are of current interest to organometallic and organic chemists.

The recent surge of investigations to the chemistry of transition metal nitrosyls by inorganic biochemists and biologists is largely due to the Nobel Prize winning discovery [30–33] that endothelium-derived relaxing factor is the nitric oxide and to the realization that nitric oxide is implicated in a multitude of physiological and pathophysiological functions. Nitric oxide has been shown to have many bioregulatory functions [34] in mammalian including cardiovascular control, neuronal signaling and an agent for defense mechanism against microorganism and tumours. As a result of these diverse and important applications many books, reviews and special topic papers are devoted to transition metal nitrosyl chemistry [35].

The dinitrosyl compounds of molybdenum have gained considerable interest due to their applicability as homogeneous catalysts [36–38]. Some dinitrosylmolybdenum(0) complexes were reported [29] to be used as catalysts in isomerization reactions of alkenes. Certain dinitrosyl complexes [29] of transition metals were found to catalyze the conversion of CO and NO to the less harmful gases CO₂ and N₂O, which is of intrinsic interest because of their environmental relevance. It is recently reported by Keller and Matusiak [39] that [Mo(NO)₂(OCR)₂ – Lewis acid] catalysts (Lewis acid = TiCl₄, SnCl₄, EtAlCl₂; R = phenyl, methylvaleric, ethylhexanoic) induce monosubstituted acetylenes (phenylacetylene, *tert*-butylacetylene) to polymerize. The catalytic ability of these catalysts strongly depends on the Lewis acid and solvent.

The widely applied routes to prepare dinitrosylmolybdenum(0) complexes are: (i) the reactions of $[{Mo(NO)_2X_2}_n]$ (X = halogens) with ligands [40] and (ii) the reactions of nitrosyl halides with molybdenum hexacarbonyl or its derivatives [41]. Bencze et al. [42] have generated dinitrosylmolybdenum(0) species by the reductive reaction of nitric oxide with molybdenum pentachloride. The generation of dinitrosylmolybdenum(0), $[Mo(NO)_2]^{2+}$ moiety, from ammonium heptamolybdate in aqueous-aerobic conditions [in slightly basic medium (dimethylformamide)] and its stabilization using mono- and bidentate ligands has been reported by Sarkar and Subramanian [43]. Following the method of Sarkar and Subramanian, Perpinan et al. [44] carried out the reaction of the $[Mo(NO)_2]^{2+}$ moiety with X,Y-donor (mixed coordination sites) ligands (X, Y = dithiocarbamates, xanthates, 2-picolinate,o-aminophenoxide, o-aminothiophenoxide or dithizone), which led to the formation of complexes of the type $[Mo(NO)_2(X,Y)_2]$. Complexes of the type $[Mo(NO)_2$ $(HA)_2$], where H_2A = benzohydroxamic acid or salicylhydroxamic acid, have been isolated and characterized by Bag and co-workers [45]. The complexes have been prepared by reductive nitrosylation of ammonium heptamolybdate by hydroxylamine hydrochloride in the presence of H₂A under aqueous-aerobic conditions.

The synthesis and characterization of several dinitrosylmolybdenum(0) complexes using $[Mo(NO)_2(CN)_4]^{2-}$ [46–48] and $[Mo(NO)_2(acac)_2]$ (acacH = acetylacetone) [49,50] as precursors^{8–12} have been carried out in our laboratory. Maurya et al. [51] have recently reported the synthesis and characterization of some dinitrosylmolybdenum(0) complexes involving 4-butyryl-3-methyl-1-phenyl-2-pyrazolin-5-one and its Schiff bases with *o*-phenetidine, *p*-ansidine, *o*-phenylenediamine and *m*-phenylenediamine, for the first time, using $[Mo(NO)_2]^{2+}$ moiety [43] as precursor. The ligational behaviour of 8-hydroxysulphonamides [20] towards $[Mo(NO)_2]^{2+}$ has also been examined by Maurya et al.

In view of the diverse and important applications of transition metal nitrosyl compounds, and also extending the search for new dinitrosylmolybdenum(0) complexes, we have studied the reactivity of $[Mo(NO)_2]^{2+}$ (generated by the method of Sarkar and Subramanian, Ref. [43]) towards some Schiff bases derived from pyrazolone based carbonyl compounds and amine of the same family, not reported hitherto. Some dinitrosylmolybdenum(0) complexes of the Schiff bases, such as, N-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)-4-aminoantipyrine (mphyp-aap H), N-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-4aminoantipyrine (bmphp-aapH), N-(3'-methyl-1'-phenyl-4'-propionylidene-2'-pyrazolin-5'-one)-4-aminoantipyrine (mphpp-aapH), N-(4'-acetylidene-3'-methyl-1'-phenyl-2'pyrazolin-5'-one)-4-aminoantipyrine (amphp-aapH) or N-(-4'-iso-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5one)-4-aminoantipyrine (iso-bumphp-aapH), have thus been isolated directly from ammonium heptamolybdate in a single-step process and the results of our investigation are reported here.

2. Experimental

2.1. Materials

Ammonium heptamolybdate tetrahydrate (Aldrich chemical Co., USA), hydroxylamine hydrochloride (Sisco Chem. Pvt. Ltd, Mumbai), 4-aminoantipyrine (BDH Chemicals, Mumbai), valeryl chloride, *iso*-butyryl chloride (Fluka Chemie, Switzerland), 3-methyl-1-phenyl-2-pyrozo-line-5-one (Johnson Chemical Co., Bombay), benzoyl chloride, acetyl chloride and propionyl chloride (Thomas Baker Chemicals. Ltd, Mumbai) were used as supplied. All other chemicals used were of AR Grade.

2.2. Preparation of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one (pyrazolone based carbonyl compounds)

4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (bmphp) was prepared by the interaction of 3-methyl-1-phenyl-2-pyrozoline-5-one in dioxane with calcium hydroxide and benzoyl chloride by the procedure reported by Jensen [52] and was recrystallised from a methanol-water (9:1) mixture. Analytical data calculated for $C_{17}H_{14}N_2O_2$: C = 73.35%, H = 5.07%, N = 10.06%, Found: C = 73. 56%, H = 5.20%, N = 10.03%. IR data: ν (C=O)

(side chain) 1645 cm⁻¹, v(C=O) (ring) 1600 cm⁻¹, v(C=N)(pyrazolone ring) 1566 cm⁻¹. ¹H NMR data: δ 7.32– 7.96 ppm (M, 10H, aromatic), δ 2.60 ppm (S, 1H, --CH), δ 1.50 ppm (S, 3H, --CH₃). Following the same procedure, 3-methyl-1-phenyl-4-valeryl-2-pyrazolin-5-one (mphvp), 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one (mphpp), 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one (amphp) and 4-*iso*-butyryl-3-methyl-1-phenyl-4-pyrazolin-5-one (*iso*-bumphp) were prepared using valeryl chloride, propionyl chloride, acetyl chloride and *iso*-butyryl chloride, respectively. The reaction scheme related to the synthesis of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one is as follows:



3-Methyl-1-phenyl-2-pyrazolin-5-one



4-Acyl-3-methyl-1-phenyl-2-pyrazolin-5-one

2.3. Preparation of Schiff base ligands

The Schiff base ligands were prepared [53] by taking 1:1 ethanolic solution of mphyp (2.58 g, 10 mmol), bmphp (2.78 g, 10 mmol), mphpp (2.30 g, 10 mmol), amphp (2.16 g, 10 mmol) or *iso*-bumphp (2.44 g, 10 mmol) and 4-aminoantipyrine (2.03 g, 10 mmol) and refluxing the resulting solution for 5–7 h. The reaction mixture was then poured into distilled water (250 mL) when a yellow precipitate was obtained. It was filtered, washed several times with water and then dried in vacuo. The characterization data of the Schiff base ligands are given in Table 1.

2.4. Synthesis of dinitrosylmolybdenum(0) complexes

tetrahydrate Ammonium heptamolybdate (1 g, 0.8 mmol) and hydroxylamine hydrochloride (1.7 g, 24.4 mmol) were heated in 10 mL DMF at 90 °C for 1 h to produce a green solution [43]. Into this green solution was added a solution of mphvp-aapH (2.215 g, 5 mmol), bmphp-aapH (2.315 g, 5 mmol), mphpp-aapH (2.075 g, 5 mmol), amphp-aapH (2.005 g, 5 mmol) or iso-bumphpaapH (2.145 g, 5 mmol) in \sim 40 mL ethanol. The resulting solution was refluxed for 8-10 h. The solution was concentrated on a water bath and kept overnight, when coloured solid was obtained. It was filtered by suction and washed several times with 1:5 ethanol water and then

	-				, ;			1		i		1
Compound	Schiff base (empirical formula)	Found (Calcd), %		Colour	Yield (%)	Decom.	v(C=0)	v(C=N)	v(C≡N)	۷(OH)	v (C-0)
No.	(formula weight)	С	Н	Z			temp. (°C)	(ketoic)	(azomethine)	(cyclic)		(enolic)
(1)	mphvp-aapH (C ₂₆ H ₂₉ N ₅ O ₂) (443)	70.25 (70.43)	6.62 (6.55)	15.58 (15.80)	Mustered yellow	54	120	1666 s	1635 s	1584 s	3425 br	1155 m
(II)	bmphp-aapH (C ₂₈ H ₂₅ N ₅ O ₂) (463)	72.46 (72.57)	5.68 (5.40)	15.36 (15.12)	Canary yellow	52	140	1670 s	1643 s	1583 s	3422 br	1155 m
E	mphpp-aapH $(C_{24}H_{25}N_{5}O_{2})$ (415)	69.25 (69.40)	6.18 (6.02)	16.99 (16.87)	Golden yellow	52	170	1669 s	1632 s	1589 s	3423 br	1162 m
(IV)	amphp-aapH $(C_{23}H_{23}N_{5}O_{2})$ (401)	68.64 (68.83)	5.64 (5.74)	17.28 (17.46)	Light brown	50	140	1674 s	1625 s	1585 s	3419 w	1129 m
$\mathbf{\hat{s}}$	<i>iso</i> -bumphp-aapH ($C_{25}H_{27}N_{5}O_{2}$) (429)	69.74 (69.93)	6.11 (6.29)	16.13 (16.32)	Sand stone	50	160	1670 s	1630 s	1585 s	3440 br	1132 m
mphvp-aap aap $H = N$ -(, N -(M - M -(M - M -(M - M - M -(M - M - M -(M - M - M - M -(M - M - M - M - M -(M - M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M -(M - M - M - M - M -(M - M - M -(M - M - M -(M - M - M - M -(M - M - M -(M - M - M -(M - M - M - M -(M - M - M -(M - M - M - M -(M - M - M - M -(M - M - M -(M - M - M -(M - M - M - M -(M - M - M -(M - M - M - M -(M - M - M -(M - M - M - M -(M - M -(M - M -(M - M - M -(M - M -(M - M - M -(M - M - M -(M - M -(M - M - M -(M - M - M -(M - M -(M - M -(M - M -(M - M - M -(M - M -(M - M - M -(M - M -(M - M - M -(M - M -(M - M - M -(M - M -(M - M - M -(M - M - M -(M -(H = N-(3'-methyl-1'-phenyl-4'-valerylidene- 3'-methyl-1'-phenyl-4'-propionylidene-2'-pyri vuvidene-3'-methyl-1',-n-benyl-2'-avrazolin-5'	-2'-pyrazolin-5'- razolin-5'-one)-4- 5'-one)-4-aminoa	one)-4-aminos aminoantipyr	antipyrine; bm ine; amphp-aaj	php-aap $H = N-(4'-$ o $H = N-(4'-$ acetylide	benzoylidene ene-3'-methyl	-3'-methyl-1' -1'-phenyl-2'-	-phenyl-2'- ₁ pyrazolin-5'	yrazolin-5'-on -one)-4-aminoa	e)-4-aminoa ntipyrine;	intipyrine; iso-bumph	mphpp- o-aapH =

Table

dried in vacuo. The analytical data of complexes are given in Table 2.

2.5. Analyses

Carbon, hydrogen and nitrogen were determined microanalytically on Heraeus Carlo Erba 1108 elemental analyzer. The molybdenum content in each of the synthesized complexes was determined gravimetrically as $MoO_2(-C_9H_6ON)_2$ by the method reported elsewhere [54].

2.6. Chemical identification of the coordinated nitrosyl group

The identification of the coordinated nitrosyl group in the resulting complexes was made by the chemical method reported by Maurya [6]. Each nitrosyl compound under the present investigation was decomposed with KOH followed by acidifying with acetic acid. The resulting filtrate was added with few drops of the Griess Reagent [55]. The appearance of a pink colour indicated the coordination of nitric oxide as NO⁺ in the complex. The principle involved in this method is the use of the electrophilic behaviour of the coordinated NO group in the metal nitrosyls. The linearly bonded M—N—O group may be assumed to contain "NO⁺" which can react with strong alkali to produce NO₂⁻.

 $2NO^+ + 4OH^- \rightarrow 2NO_2^- + 2H_2O$

The resulting NO_2^- gives a pink colour [55] with the Griess reagent.

2.7. Physical methods

Electronic spectra of the complexes were recorded in dimethylformamide on an ATI Unicam UV-1-100 UV-visible spectrometer in our laboratory. Magnetic measurements were performed by vibrating sample magnetometer method at RSIC, IIT, Chennai. Solid state infrared spectra were obtained using Perkin-Elmer model 1620 FT-IR Spectrometer on KBr disc at CDRI, Lucknow. Conductance measurements were made at room temperatures in dimethylformamide using a Toshniwal conductivity bridge and dip-type cell with a smooth platinum electrode of cell constant 1.02. Decomposition temperatures of the Schiff bases and the chelates were recorded using an electrothermal apparatus having the capacity to record temperatures up to 360 °C. Thermogravimetric curves of the complexes were recorded in the temperature range 50-1000 °C at the heating rate of 15 °C/min. using a Mettler Toledo Star^e System at the Regional Sophisticated Instrumentation Centre, Nagpur.

2.8. Molecular modeling studies

The 3D molecular modeling of a representative compound was carried out on a CS Chem 3D Ultra Molecular Modeling and Analysis Programme [56]. It an interactive

Table 2									
Analytical data	and some physical properties of the synthesized complexes								
Compound No.	Compound (empirical formula) (formula weight)	Found (Calcd.	.), %			Colour	Yield (%)	Decom.	$\Lambda_{m(Ohm^{-1})}$
		С	Н	N	Mo			temp. (°C)	$cm^2 mol^{-1}$)
(1)	[Mo(NO) ₂ (mphvp-aap)(OH)] (C ₂₆ H ₂₉ MoN ₇ O ₅) (614.94)	50.94 (50.74)	4.52 (4.72)	15.78 (15.94)	15.31 (15.60)	Brown	55	180	45.5
(2)	$[Mo(NO)_2(bmphp-aap)(OH)] (C_{28}H_{25}MoN_7O_5) (634.94)$	52.53 (52.92)	3.80 (3.94)	15.69 (15.43)	15.43 (15.11)	Middle buff	50	160	40.2
(3)	[Mo(NO) ₂ (mphpp-aap)(OH)] (C ₂₄ H ₂₅ MoN ₇ O ₅) (586.94)	49.28 (49.07)	4.32 (4.26)	16.83 (16.70)	16.13 (16.35)	Middle buff	50	200	25.3
(4)	[Mo(NO) ₂ (amphp-aap)(OH)] (C ₂₃ H ₂₃ MoN ₇ O ₅) (572.94)	48.35 (48.17)	4.22(4.01)	17.23 (17.10)	16.49 (16.75)	Golden yellow	55	170	30.7
(5)	$[Mo(NO)_2(iso-bumphp-aap)(OH)] (C_{25}H_{27}MoN_7O_5) (600.94)$	49.61 (49.92)	4.64 (4.49)	16.12 (16.31)	15.74 (15.96)	Golden yellow	55	200	44.8

graphics programme that allows rapid structure building, geometry optimization with minimum energy and molecular display. It has ability to handle transition metal compounds.

3. Results and discussion

3.1. Characterization of Schiff base ligand

The pyrazolone based Schiff base ligands in the present investigation were prepared as shown in Scheme 1.

The formation of the Schiff base ligands is consistent with the microanalytical data of the ligands. The microanalytical data, melting points, colours, % yields and important IR spectral bands are given in Table 1. The formation of Schiff base ligands is supported by the appearance of a strong band at $1625-1643 \text{ cm}^{-1}$ due to v(C=N) (azomethine) in the IR spectra of these ligands [53]. The appearance of a broad band due to v(OH) centred at 3419–3440 suggests that these ligands exist in enol form in the solid

state. This is further supported by the presence of a medium band at $1132-1162 \text{ cm}^{-1}$ assignable to v(C-O) (enolic) [57].

3.2. Characterization dinitrosylmolybdenum(0) complexes

The dinitrosylmolybdenum(0) chelates of 4-aminoantipyrine Schiff bases under this investigation were prepared according to the reaction Scheme 2.

The resulting compounds are air-stable coloured solids. Some physical properties of the complexes are given in Table 2. They were characterized by the following physical studies.

3.3. Infrared spectral studies

The important infrared spectral bands of the complexes along with their tentative assignments are given in Table 3. All the ligands used in the present investigation exist in enol form (vide supra). Hence, they possess seven potential



Scheme 1. Synthesis of Schiff base ligands.

DMF $7[Mo(NO)_2]^{2+}$ + other products (NH₄)₆Mo₇O₂₄.4H₂O + NH₂OH.HCl (Excess) (1)(1.0g; 0.809 mmol) (1.7g) 90 °C 5.6 mmol (Green solution) Ethanol, H₂O $[Mo(NO)_2]^{2+} + LH$ $[Mo(NO)_2(L)(OH)] + 2H^+$ (2) 5.6 mmol 5 mmol Reflux, 8-10 h Where LH = mphyp-aapH(1), bmphp-aapH(2), mphpp-aapH(3), amphp-aapH(4) or iso-bumphp-aapH (5)

Table 3 Important IR spectral bands (cm⁻¹) of the synthesized complexes

Compound No.	Compound	$v(NO)^+$	v(C=O) (ketonic)	v(C=N) (azomethine)	v(C—O) (enolic)	v(OH)	v(Mo–NO)
(1)	[Mo(NO) ₂ (mphvp-aap)(OH)]	1780 s 1655 s	1582 s	1605 s	1174 m	3430 br	625 w
(2)	$[Mo(NO)_2(bmphp-aap)(OH)]$	1773 s 1645 s	1575 s	1598 s	1164 m	3428 br	621 w
(3)	[Mo(NO) ₂ (mphpp-aap)(OH)]	1774 s 1653 s	1575	1602 s	1174 m	3413 br	620 w
(4)	[Mo(NO) ₂ (amphp-aap)(OH)]	1775 s 1650 s	1581 s	1604 s	1186 m	3410 br	656 w
(5)	[Mo(NO) ₂ (<i>iso</i> -bumphp-aap)(OH)]	1772 s 1650 s	1584 s	1608 s	1165 m	3430 br	630 w

donor sites: (i) and (ii) the ring nitrogens, N_1 , (iii) and (iv) the ring nitrogens, N_2 , (v) the enolic oxygen of 2-pyrazolin-5-one skeleton, (vi) the cyclic carbonyl oxygen of 3-pyrazolin-5-one skeleton and (vii) azomethine nitrogen. The coordination of the ring nitrogens N_1 is unlikely because of the presence of a bulky phenyl group attached to it in 2- and 3-pyrazolin-5-one skeletons. Coordination of N_1 of 3-pyrazolin-5-one skeleton is also unfavourable due to the possible Zwitterion [58] formation on account of cyclic amide group and thereby lowering the basidity of N_1 as shown below in Scheme 3.

Considering the planarity of the ligands, the coordination of ring nitrogens, N_2 , is also unlikely due to being back side of the suitable donor sites (v), (vi), (vii) with reference to the details of donor sites given above. Moreover, the coordination of the ring nitrogen N_2 of 3-pyrazolin-5-one skeleton is also unfavourable due to the possible zwitterion [58] formation on account of conjugation and thereby lowering the basidity of N_2 as shown below in Scheme 4.

The ring nitrogen N₂ in these ligands is found to be inert towards coordination to molybdenum as revealed by no change in $v(C=N_2)$ (1583–1589 cm⁻¹) of the free ligands after complexation. In fact, $v(C=N_2)$ mode seems to be merged with v(C=O) (cyclic) mode in the respective complexes.

For a carbonyl donor, a significant shift of v(C=O) to lower wave number takes place because of the coor-



Scheme 3. Zwitterion formation due to cyclic amide in 3-pyrazolin-5-one skeleton.



Scheme 4. Zwitterion formation due to conjugation in 3-pyrazolin-5-one skeleton.

dination through carbonyl oxygen. The v(C=O) for the cyclic carbonyl group at 1666,1670,1669, 1674 and 1670 cm⁻¹ in uncoordinated mphvp-aapH, bmphp-aapH, mphpp-aapH, amphp-aapH and *iso*-bumphp-aapH, respectively, is shifted to lower wave numbers and appears at 1582, 1575, 1575, 1581 and 1584 cm⁻¹ in the respective complexes. This indicates that the cyclic carbonyl oxygen [59] is bonded to molybdenum in these complexes.

The IR spectra of these ligands exhibit a strong band at $1630-1643 \text{ cm}^{-1}$ assignable to v(C=N) (azomethine). In the spectra of the respective complexes this band is shifted to lower frequency [60] (see Table 3), suggesting the coordination of the azomethine nitrogen to the metal centre.

In all the complexes, the absence of a broad band centred at $3419-3440 \text{ cm}^{-1}$ and the presence of a medium band at $1164-1186 \text{ cm}^{-1}$ due to v(C-O) (enolic) indicate the deprotonation and coordination of enolic oxygen [53] to the metal centre.

The appearance of two strong bands in the region 1772–1780 and 1645–1655 cm⁻¹ and a weak band at 620–656 cm⁻¹ may be assigned to $v(NO)^+$ and v(MO-NO), respectively, which are in agreement with previously reported results [61,62]. The appearance of two v(NO) bands in the spectra of all the synthesized complexes suggests the presence of a *cis*-[Mo(NO)₂]²⁺ moiety [61,63] in the complexes. The appearance of v(OH) mode at 3410–3430 cm⁻¹ in all the complexes

under study is most probably due to presence of a coordinated hydroxy group. The IR spectra of a representative Schiff base ligand, mphpp-aapH (III), and its complex, [Mo(NO)₂(mphpp-aap)(OH)] (3), are given in Figs. 1 and 2, respectively.

3.4. Conductance measurements

The molar conductances measured in 10^{-3} M DMF solutions of these complexes are in the range 25.3-45.4 Ω^{-1} cm² mol⁻¹ and thereby indicate the non-electro-



lytic nature of these complexes [64]. The high molar conductance values are most probably due to strong donor capacity of dimethylformamide, which may lead to the displacement of anionic ligands and change of electrolyte [64] type.

3.5. Magnetic measurements

The magnetic susceptibility measurements of these complexes indicate that they are diamagnetic and, hence, they should have ground states with a molecular orbital configuration $({}^{1}a_{2})^{2}$ $({}^{1}a_{1})^{2}$ and $({}^{1}b_{2})^{2}$ following the molecular orbital diagram reported elsewhere [4]. This result is consistent with the low-spin {Mo(NO)₂}⁶ electron configuration of Mo(0) in these complexes. The diamagnetic and nonelectrolytic nature of these complexes also supports the presence of two NO⁺ groupings in all of these complexes.

3.6. Thermogravimetric analyses

Two compounds, namely, $[Mo(NO)_2(bmphp-aap)(OH)]$ (2) and $[Mo(NO)_2(mphpp-aap)(OH)]$ (3), were subjected to thermogravimetric analysis in the temperature range 50–1000 °C at the heating rate of 15.8 °C min⁻¹. The compound (2) shows a weight loss of 2.64% at 146 °C corresponding to the elimination of one hydroxo group from the complex (calcd. 2.67%). This compound shows six more weight losses at different temperatures which we could not correlate separately. However, the weight loss observed (83.77%) at ~782 °C corresponds to the elimination of one hydroxo-, two nitrosyl-, and one ligand-group(s) against a theoretical weight loss of 84.88%.

The first weight loss of 2.65% displayed by the compound (3) at 150 °C corresponds to the elimination of one hydroxo group from the complex (calcd. 2.89%). Similar to compound (2), this compound also exhibits six more weight losses, which we again could not correlate separately. However, the weight loss observed (83.5%) at ~715 °C corresponds to the elimination of one hydroxo-, two nitrosyl-, and one ligand-group(s) from the complex (calcd. 83.65%). The thermograms of these two compounds, therefore, corroborate some of the assumptions made on the basis of infrared spectral studies for these complexes (vide supra).

Table 4	ŀ
---------	---

Electronic	spectral	data	of	some	compl	exes

Compound No.	Compound	$\lambda_{Max} (nm)$	$\varepsilon (L \text{ mol}^{-1} \text{ cm}^{-1})$	Peak assignment
(1)	[Mo(NO) ₂ (mphvp-aap)(OH)]	298	5265	${}^{1}b_2 \rightarrow {}^{2}b_1$
		338	5520	${}^{1}b_{2} \rightarrow {}^{2}a_{2}$
		365	5914	${}^{1}b_2 \rightarrow {}^{3}a_1$
		393	3747	${}^{1}b_2 \rightarrow {}^{2}b_2$
		417	3634	${}^{1}b_{2} \rightarrow {}^{1}b_{1}$
		720	745	${}^{1}b_{2} \rightarrow {}^{2}a_{1}$
(2)	$[Mo(NO)_2(bmphp-aap)(OH)]$	289	4390	${}^{1}b_{2} \rightarrow {}^{2}a_{2}$
		313	4315	${}^{1}b_{2} \rightarrow {}^{3}a_{1}$
		339	5221	${}^{1}b_{2} \rightarrow {}^{2}b_{2}$
		357	5409	${}^{1}b_{2} \rightarrow {}^{1}b_{1}$
		416	3052	${}^{1}b_{2} \rightarrow {}^{2}a_{1}$
(3)	$[Mo(NO)_2(mphpp-aap)(OH)]$	295	4411	${}^{1}b_{2} \rightarrow {}^{2}a_{2}$
		316	4666	${}^{1}b_{2} \rightarrow {}^{3}a_{1}$
		351	5141	${}^{1}b_2 \rightarrow {}^{2}b_2$
		365	5054	${}^{1}b_{2} \rightarrow {}^{1}b_{1}$
		457	3480	${}^{1}b_2 \rightarrow {}^{2}a_1$
(4)	$[Mo(NO)_2(amphp-aap)(OH)]$	293	4110	${}^{1}b_{2} \rightarrow {}^{2}b_{1}$
		329	5255	${}^{1}b_2 \rightarrow {}^{2}a_2$
		356	5046	${}^{1}b_2 \rightarrow {}^{3}a_1$
		387	3021	${}^{1}b_2 \rightarrow {}^{2}b_2$
		444	2722	${}^{1}b_{2} \rightarrow {}^{1}b_{1}$
		705	166	${}^{1}b_2 \rightarrow {}^{2}a_1$
(5)	[Mo(NO) ₂ (<i>iso</i> -bumphp-aap)(OH)]	274	3722	${}^{1}b_2 \rightarrow {}^{2}a_2$
		296	4312	${}^{1}b_2 \rightarrow {}^{3}a_1$
		325	4582	${}^{1}b_2 \rightarrow {}^{2}b_2$
		349	4821	${}^{1}b_{2} \rightarrow {}^{1}b_{1}$
		440	1942	${}^{1}b_2 \rightarrow {}^{2}a_1$
Ref. 43	$Mo(NO)_2(o-AP)_2$	280	10,798	π^* (NO) \leftarrow M charge transfer
		325	2264	π^* (NO) \leftarrow M charge transfer
		475	2667	$d \leftarrow d$
		650	179	$d \leftarrow d$
Ref. 43	$[Mo(NO)_2(2-pic)_2]$	296	5372	π^* (NO) \leftarrow M charge transfer
		433	433	π^* (NO) \leftarrow M charge transfer
		655	296	$d \leftarrow d$

3.7. Electronic spectral studies

Electronic spectra of complexes were recorded in 10^{-3} M DMF solutions. The electronic spectral peaks observed in each of the complexes along with their molar extinction coefficients are presented in Table 4. The compounds 1 and 6 in the present investigation display six transitions while compounds 2, 3 and 5 exhibit only five transitions. The assignments of these transitions are given in Table 4, and are based on molecular orbital diagram applicable to hexa-coordinated dinitrosyl complexes reported elsewhere [4]. These observations are in agreement with the results reported by Perpinan et al. [44], for some dinitrosylmolybdenum(0) complexes.

3.8. 3D molecular modeling and analysis

In view of the hexa-coordination of the present complexes (vide infra, Section 4), the molecular modeling of compound, $[Mo(NO)_2(bmphp-aap)(OH)]$ (2) as a representative, is based on its octahedral structure. The details of bond lengths and bond angles as per the 3D structure (Fig. 3) are given in Tables 5 and 6, respectively. For convenience of looking over the different bond lengths and bond angles, the various atoms in the compound in question are numbered in arabic numerals. In all, 198 measurements of the bond lengths (72 in numbers), plus the bond angles (126 in numbers) are listed in Tables 5 and 6. Except few cases, optimal values of



Fig. 3. 3D structure of [Mo(NO)₂(bmphp-aap)(OH)] (2).

Table 5 Various bond lengths of compound [Mo(NO)₂(bmphp-aap)(OH)] (2)

C NL	A	A., .11	0 (11 11 11	5. 140.	Atoms	Actual
5. NO.	Atoms	Actual bond length	Optimal bond length	66	N(4) - N(5)	1.6235
1	O(41) - N(40)	1.1318	-	67	Mo(24)-O(3)	1.94
2	C(39)—H(66)	1.1	1.1	68	N(4) - C(2)	1.266
3	C(39) - C(38)	1.337	1.42	69	C(2) - O(3)	2.8446
4	H(65) - C(37)	1.1	1.1	70	C(1) - N(15)	1.266
5	C(38) - C(37)	1.337	1.42	71	C(1) - C(7)	1.337
6	H(64) - C(36)	11	11	72	C(1) - C(2)	1 337
7	C(37) - C(36)	1 337	1 42	12	C(1) $C(2)$	1.557
, o	C(37) = C(30) C(35) = H(63)	1.557	1.1			
0	$C(35) = \Gamma(05)$ C(25) = C(26)	1.1	1.1			
9	U(33) - U(30)	1.55/	1.42	Table 6		
10	H(62) - C(34)	1.1	1.1	Various l	bond angles of co	ompound
11	C(39) - C(34)	1.337	1.42	S No	Atoms	
12	C(35)-C(34)	1.337	1.42	5. 110.	1 101115	
13	C(33) - H(61)	1.1	1.1			
14	C(32) - H(60)	1.1	1.1	1	H(64)-C(36)	-C(37)
15	C(33) - C(32)	1.337	1.42	2	H(64)-C(36)	-C(35)
16	H(59)-C(31)	1.1	1.1	3	C(35)-C(36)	-C(37)
17	C(32) - C(31)	1.337	1.42	4	H(63)-C(35)	-C(36)
18	H(58)-C(30)	1.1	1.1	5	H(63)-C(35)	-C(34)
19	C(30) - C(31)	1.337	1.42	6	C(36) - C(35)	-C(34)
20	C(29) - H(57)	1.1	1.1	7	C(39) - C(34)	-H(62)
21	C(29) - C(30)	1 337	1.42	8	C(35) - C(34)	-H(62)
22	C(33) - C(28)	1 337	1 42	9	C(39) - C(34)	-C(35)
22	C(29) - C(28)	1 337	1.42	10	C(38) - C(39)	-H(66)
23	U(25) = U(20) U(56) = O(27)	0.042	0.042	10	U(56) - C(39)	-C(24)
24	N(26) - O(27)	0.942	0.942	11	$\Gamma(00) - C(39)$ C(28) - C(20)	-C(34)
25	N(20) = O(23)	1.1510	—	12	$C(38) - C(39)^{-1}$	-0(34)
20	MO(24) - N(40)	1.976	-	13	H(65) - C(37)	-C(38)
27	N(26) - Mo(24)	1.9/6	_	14	H(65)-C(37)	-C(36)
28	Mo(24)—O(27)	1.94	-	15	C(38) - C(37)	-C(36)
29	C(23)-C(28)	1.337	1.503	16	C(33) - C(32)	-H(60)
30	H(54)-C(22)	1.113	1.113	17	H(60)-C(32)	-C(31)
31	C(22) - H(55)	1.113	1.113	18	C(33) - C(32)	-C(31)
32	H(53)-C(22)	1.113	1.113	19	H(59)-C(31)	-C(32)
33	Mo(24)-O(21)	1.1464	_	20	H(59)-C(31)	-C(30)
34	C(20) - O(21)	1.355	1.355	21	C(32) - C(31)	-C(30)
35	C(19) - C(23)	1.337	1.503	22	H(58)-C(30)	-C(31)
36	C(19) - C(20)	1.337	1.337	23	C(29) - C(30)	-H(58)
37	C(22) - C(18)	1.497	1.497	24	C(29) - C(30)	-C(31)
38	C(19) - C(18)	1.337	1.503	25	C(32) - C(33)	-H(61)
39	C(18) - N(17)	1.26	1.26	26	H(61)-C(33)	-C(28)
40	C(38) - N(16)	1 266	1 462	20	C(32) - C(33)	-C(28)
41	C(20) - N(16)	1.266	1.462	28	H(57) - C(29)	-C(30)
42	N(17) - N(16)	1.614	1 426	20	H(57) - C(29)	-C(28)
13	$N(15) - M_0(24)$	1.076	1.420	30	C(30) - C(29)	-C(28)
43	N(15) - N(0(24)) N(15) - C(22)	1.970	-	30	C(30) - C(29)	-C(20)
44	N(13) = C(23)	1.200	1.200	31	C(39) - C(38)	$-\mathbf{U}(3)$
45	U(14) - H(52)	1.1	1.1	32	C(39) - C(38)	-N(16)
46	H(51) - C(13)	1.1	1.1	33	C(37) - C(38)	-N(16)
4/	C(14) - C(13)	1.33/	1.42	34	H(54)-C(22)	-H(55)
48	C(12) - H(50)	1.1	1.1	35	H(54)-C(22)	-H(53)
49	C(13)-C(12)	1.337	1.42	36	H(54)-C(22)	-C(18)
50	C(11) - H(49)	1.1	1.1	37	H(53)-C(22)	-H(55)
51	C(11)-C(12)	1.337	1.42	38	C(18) - C(22)	-H(55)
52	C(10) - H(48)	1.1	1.1	39	H(53)-C(22)	-C(18)
53	C(10) - C(11)	1.337	1.42	40	C(18)-N(17)	-N(16)
54	C(9) - C(14)	1.337	1.42	41	C(38)-N(16)	-C(20)
55	C(10) - C(9)	1.337	1.42	42	C(38)-N(16)	-N(17)
56	C(8) - H(47)	1.113	1.113	43	C(20) - N(16)	-N(17)
57	C(8)—H(46)	1.113	1.113	44	C(19) - C(20)	-O(21)
58	C(8) - H(45)	1.113	1.113	45	O(21) - C(20)	-N(16)
59	C(8) - C(7)	1 497	1 497	46	C(10) - C(20)	-N(16)
60	C(6) - H(42)	1 113	1 113	40	$C(22) = C(20)^{2}$	-C(10)
61	H(44) - C(6)	1.113	1.113		$C(22) = C(10)^{-1}$	-N(17)
62	C(6) = U(42)	1.113	1.113	40 40	$C(10) = C(18)^{-1}$	-1N(17)
62	V(0) = H(43)	1.113	1.113	49	U(19) - U(18)	-in(1/)
03	N(5) - C(6)	1.4/	1.4/	50	H(51)-C(13)	-C(14)
64	N(5) - C(7)	1.266	1.462	51	H(51)-C(13)	-C(12)
65	N(4) - C(9)	1.266	1.462	52	C(14) - C(13)	-C(12)

Table 5	(continued)

	()		
S. No.	Atoms	Actual bond length	Optimal bond length
66	N(4)-N(5)	1.6235	-
67	Mo(24)-O(3)	1.94	-
68	N(4) - C(2)	1.266	1.462
69	C(2) - O(3)	2.8446	1.355
70	C(1) - N(15)	1.266	1.462
71	C(1) - C(7)	1.337	1.337
72	C(1)-C(2)	1.337	1.503

Fable 6 Various t	oond angles of compound []	Mo(NO)2(bmphp-a	ap)(OH)] (2)
S No	Atoms	Actual bond	Optimal bond
		angles	angles
1	H(64) - C(36) - C(37)	120.0001	120
2	H(64)-C(36)-C(35)	119.9998	120
3	C(35) - C(36) - C(37)	120.0001	_
4	H(63) - C(35) - C(36)	120.0006	120
5	H(63) - C(35) - C(34)	119.9995	120
6	C(36) - C(35) - C(34)	119.9999	_
7	C(39)-C(34)-H(62)	120.0001	120
8	C(35)-C(34)-H(62)	120.0001	120
9	C(39)-C(34)-C(35)	119.9998	_
10	C(38)-C(39)-H(66)	120	120
11	H(66)-C(39)-C(34)	119.9998	120
12	C(38)-C(39)-C(34)	120.0002	-
13	H(65)-C(37)-C(38)	120.0001	120
14	H(65)-C(37)-C(36)	119.9997	120
15	C(38)-C(37)-C(36)	120.0001	_
16	C(33)-C(32)-H(60)	120.0003	120
17	H(60)-C(32)-C(31)	119.9997	120
18	C(33)-C(32)-C(31)	120	_
19	H(59)-C(31)-C(32)	120.0005	120
20	H(59)-C(31)-C(30)	119.9995	120
21	C(32)-C(31)-C(30)	120	_
22	H(58) - C(30) - C(31)	120.0001	120
23	C(29)-C(30)-H(58)	120	120
24	C(29)-C(30)-C(31)	119.9999	_
25	C(32)-C(33)-H(61)	120.0002	120
26	H(61)-C(33)-C(28)	119.9994	120
27	C(32)-C(33)-C(28)	120.0003	_
28	H(57)-C(29)-C(30)	119.9999	120
29	H(57)-C(29)-C(28)	120.0002	120
30	C(30)-C(29)-C(28)	120	-
31	C(39)-C(38)-C(37)	119.9999	120
32	C(39)-C(38)-N(16)	119.9999	120
33	C(37)-C(38)-N(16)	120.0002	120
34	H(54)-C(22)-H(55)	109.5201	109
35	H(54)-C(22)-H(53)	109.4417	109
36	H(54)-C(22)-C(18)	109.4415	110
37	H(53)-C(22)-H(55)	109.4618	109
38	C(18)-C(22)-H(55)	109.4621	110
39	H(53)-C(22)-C(18)	109.5001	110
40	C(18) - N(17) - N(16)	103.7077	115
41	C(38)-N(16)-C(20)	128.353	124
42	C(38)-N(16)-N(17)	128.3535	124
43	C(20)-N(16)-N(17)	103.2934	124
14	C(19)-C(20)-O(21)	124.298	124.3
45	O(21)-C(20)-N(16)	124.6986	_
46	C(19)-C(20)-N(16)	110.9999	120
47	C(22)-C(18)-C(19)	124.5	121.4
48	C(22)-C(18)-N(17)	124.5002	115.1
19	C(19)-C(18)-N(17)	110.9998	120
50	H(51)-C(13)-C(14)	120.0002	120

120.0002

119.9996

120

_

S

Table 6 (continued)

S. No.	Atoms	Actual bond angles	Optimal bond angles
53	C(13)-C(12)-H(50)	119.9996	120
54	C(11)-C(12)-H(50)	120.0002	120
55	C(11)-C(12)-C(13)	120.0001	-
50 57	H(49) - C(11) - C(12) C(10) - C(11) - H(40)	120.0001	120
58	$C(10) - C(11) - \Gamma(49)$ C(10) - C(11) - C(12)	120 0003	120
50 59	C(13) - C(14) - H(52)	120.0001	120
60	C(9) - C(14) - H(52)	119.9998	120
61	C(9)-C(14)-C(13)	120.0001	_
62	C(11)-C(10)-H(48)	119.9999	120
63	H(48) - C(10) - C(9)	120.0005	120
64 (5	C(11) - C(10) - C(9)	119.9996	_
65 66	O(41) = N(40) = Mo(24) H(56) = O(27) = Mo(24)	120.0001	_
67	$M_{0}(24) = N(26) = O(25)$	110 0008	_
68	C(33) - C(28) - C(29)	119 9998	120
69	C(33) - C(28) - C(23)	120.0007	120
70	C(29) - C(28) - C(23)	119.9995	120
71	C(20)-C(19)-C(23)	120	120
72	C(18)-C(19)-C(23)	128.9983	120
73	C(18) - C(19) - C(20)	110.9992	120
74	C(19) - C(23) - C(28)	119.9996	120
75	N(15) - C(23) - C(28)	120	120
76 77	C(19)-C(23)-N(15) M ₂ (24) $C(21)$ $C(20)$	120.0004	120
// 79	MO(24) - O(21) - O(20) C(10) - C(0) - C(14)	137.6547	-
70 70	V(10) - C(9) - C(14) N(4) - C(9) - C(14)	120.0002	120
80	N(4) - C(9) - C(10)	119,9998	120
81	H(44) - C(6) - H(42)	109.4622	109
82	H(42)-C(6)-H(43)	109.4417	109
83	N(5)-C(6)-H(42)	109.4996	_
84	H(44)-C(6)-H(43)	109.5205	109
85	H(44) - C(6) - N(5)	109.4617	_
86	N(5)-C(6)-H(43)	109.4416	-
8/	H(47) - C(8) - H(46)	109.52	109
00 80	H(43) = C(8) = H(47) H(47) = C(8) = C(7)	109.4018	109
90	H(45) - C(8) - H(46)	109.4415	109
91	C(7)-C(8)-H(46)	109.4421	110
92	H(45)-C(8)-C(7)	109.4999	110
93	C(6) - N(5) - C(7)	128.3983	108
94	N(4) - N(5) - C(6)	128.3979	_
95	N(4) - N(5) - C(7)	103.2038	_
96	Mo(24) - N(15) - C(23)	119.9983	-
97	C(1) = N(15) = Mo(24)	111	-
98	C(1) = N(13) = C(23) C(8) = C(7) = N(5)	128.9982	124
100	C(8) - C(7) - N(3) C(1) - C(7) - C(8)	124.4998	125.5
100	C(1) - C(7) - N(5)	111.0003	120
102	N(26) - Mo(24) - N(40)	154.3341	_
103	O(27)—Mo(24)—N(40)	64.3341	_
104	O(21)-Mo(24)-N(40)	97.4958	_
105	N(15)-Mo(24)-N(40)	69.1324	_
106	O(3) - Mo(24) - N(40)	158.5672	_
107	N(26)- $Mo(24)$ - $O(27)N(26)$ - $Mo(24)$ - $O(21)$	90	_
108	N(26) - Mo(24) - O(21) N(26) - Mo(24) - N(15)	90.0001	-
109	$N(20) = M_0(24) = N(15)$ N(26) = M_0(24) = O(3)	44 7555	_
111	O(27) - MO(24) - O(3)	107 5296	_
112	N(15)-Mo(24)-O(27)	128,9336	_
113	O(27)-Mo(24)-O(3)	132.1742	_
114	N(15)-Mo(24)-O(21)	98.0308	_
115	O(3)-Mo(24)-O(21)	90	_
116	N(15)-Mo(24)-O(3)	90.0002	-

Table 6	(continued))
i aoie o	continuction	,

S. No.	Atoms	Actual bond angles	Optimal bond angles
117	N(5) - N(4) - C(9)	128.5478	_
118	C(9) - N(4) - C(2)	128.5474	124
119	N(5) - N(4) - C(2)	102.9047	_
120	Mo(24) - O(3) - C(2)	69.2419	-
121	N(4) - C(2) - O(3)	120.0003	_
122	N(4) - C(2) - C(1)	110.9995	120
123	C(1)-C(2)-O(3)	99.0816	124.3
124	N(15)-C(1)-C(7)	119.9999	120
125	N(15)-C(1)-C(2)	110.9998	120
126	C(7)-C(1)-C(2)	111.0001	120

both the bond lengths and the bond angles are given in the tables along with the actual ones. The actual bond lengths/bond angles given in Tables 5/6 are calculated values as a result of energy optimization in CHEM 3D Ultra, while the optimal bond length/optimal bond angle values are the most desirable/favourable (standard) bond lengths/bond angles established by the builder unit of the CHEM 3D. The missing of some values of standard bond lengths/bond angles may be due to the limitations of the software, which we had already noticed in modeling of other systems [65,66]. In most of the cases, the actual bond lengths and bond angles are close to the optimal values, and thus the proposed structures of the compound (2) as well as of the others are acceptable [65,66].

4. Conclusions

The satisfactory analytical data and all of the physico-chemical evidence presented above suggest that the present complexes are of the composition, $[Mo(NO)_2(L)(OH)]$, {where LH = N-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyr azolin-5'-one)-4-aminoantipyrine (mphvp-aapH), N-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyr azolin-5'-one)-4-aminoantipyrine (bmphp-aapH),



Fig. 4. Proposed structure of complexes.

N-(3'-methyl-1'-phenyl-4'-propionylidene-2'-pyr azolin-5'one)-4-aminoantipyrine (mphpp-aapH), N-(4'-acetylidene-3'-methyl-1'-phenyl-2'-pyr azolin-5'-one)-4-aminoantipyrine (amphp-aapH) or N-(-4'-iso-butyrylidene-3'methyl-1'-phenyl-2'-pyra zolin-5'-one)-4-aminoantipyrine (iso-bumphp-aapH), As these complexes display two peaks for vNO⁺ mode, a *cis*-octahedral structure shown in Fig. 4 has been proposed for these complexes.

Acknowledgements

The authors are thankful to Dr. S.M. Paul Khurana, Vice-chancellor of this University, for encouragement, and Professor K.K. Verma, Head, Department of Chemistry, for laboratory facilities and helpful discussion. Analytical facilities provided by the Central Drug Research Institute, Lucknow, India, and the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai, India, are gratefully acknowledged.

References

- N. Raman, A. Kulandaisamy, K. Jeyasubramanian, Indian J. Chem. 41 (2002) 942.
- [2] M. Windholz (Ed.), The Merck Index, Encyclopedia of Chemicals, Drugs and Biologicals, Merck and Co., Inc., Rahway, New Jersey, USA, 1983.
- [3] J.H. Enemark, R.D. Feltham, Coord. Chem. Rev. 13 (1974) 339.
- [4] J.H. Enemark, R.D. Feltham, in: G. Geoffroy (Ed.), Topics in Inorganic and Organometallic Stereochemistry, vol. 12, Wiley, New York, 1981, pp. 152–215.
- [5] B.L. Westcott, J.H. Enemark, in: E.I. Solomon, A.B.P. Lever (Eds.), Inorganic Electronic Spectroscopy, vol. II, Wiley, New York, 1999, pp. 403–450.
- [6] R.C. Maurya, Synthesis and Characterization of Some Novel Nitrosyl Compounds, first ed., Pioneer Publications, Jabalpur, 2000.
- [7] G.B. Richter-Addo, P. Legzdins, Metal Nitrosyl, Oxford University Press, New York, 1992.
- [8] T. Hirano, T. Oi, H. Nagao, K. Morokuma, Inorg. Chem. 42 (2003) 6575.
- [9] B.J. Coe, S.J. Glenwright, Coord. Chem. Rev. 203 (2000) 5, and references therein.
- [10] T.W. Hayton, P. Legzdins, W. Brett Sharp, Chem. Rev. 102 (2002) 935–991, and references therein.
- [11] T. Kimura, T. Sakurai, T. Shima, M. Togano, M. Mukaida, T. Nomura, Inorg. Chim. Acta 69 (1983) 135.
- [12] E. Miki, K. Harada, Y. Kamata, M. Umehara, K. Mizumachi, M. Tanaka, T. Nagai, T. Ishimori, M. Nakahara, Polyhedron 10 (1991) 583.
- [13] H. Nishimura, H. Matsuzawa, T. Togano, M. Mukaida, H. Kakihana, F. Bottomly, J. Chem. Soc. Dalton Trans. (1991) 137.
- [14] H. Tomizawa, E. Miki, K. Mizumachi, T. Ishimori, Bull. Chem. Soc. Japan 67 (1994) 1816.
- [15] R.C. Maurya, D.D. Mishra, S. Mukherjee, J. Dubey, Polyhedron 14 (1995) 1351.
- [16] R.C. Maurya, R. Verma, Indian J. Chem. 37A (1998) 147.
- [17] R.C. Maurya, V. Pillai, S. Rajput, Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 699.
- [18] R.C. Maurya, D. Sutradhar, S. Rajput, Synth. React. Inrog. Met.-Org. Chem. 33 (2003) 291.
- [19] R.C. Maurya, H. Singh, D. Sutradhar, Synth. React. Inrog. Met.-Org. Chem. 33 (2003) 581.

- [20] R.C. Maurya, A.K. Singh, Indian J. Chem. 43A (2004) 551.
- [21] L. Andrews, A. Citra, Chem. Rev. 102 (2002) 885.
- [22] A.A. Levin, J. Mol. Struct. 272 (1992) 133.
- [23] O.V. Sizova, V.I. Baranovski, N.V. Ivanova, V.V. Sizova, Mol. Phys. 101 (2003) 715.
- [24] D. Chatterjee, A. Mitra, R.E. Shepherd, R.F. Furchgott, Inorg. Chim. Acta 357 (2004) 980.
- [25] A. Katho, Z. Opre, L. Gabor, J. Ferenc, G. Lawrency, T. Goo, J. Mol. Cat. A: Chem. 204–205 (2003) 143.
- [26] D.P.S. Mingos, D.J. Sherman, in: A.J. Sykes (Ed.), Advances in Inorganic Chemistry, vol. 4, Harcourt, Brace and Jovanovich, London, 1989, pp. 293–377.
- [27] A. Miyata, M. Murakami, R. Irie, T. Katsuki, Tetrahedron Lett. 42 (2001) 7067.
- [28] W. Odenkirk, A.L. Rheingold, B. Bosnich, J. Am. Chem. Soc. 114 (1992) 6392.
- [29] K.K. Pandey, Coord. Chem. Rev. 51 (1983) 69, and references therein.
- [30] R.F. Furchgott, in: C. Owman, J.E. Hardebo (Eds.), Neural Regulation of Brain Circulation, Elsevier, New York, 1986, p. 3.
- [31] R.F. Furchgott, Ann. Rev. Pharmacol. Toxicol. 35 (1995) 1.
- [32] R.F. Furchgott, Angew. Chem., Int. Ed. 38 (1999) 1870.
- [33] L.J. Ignarro, Nitric Oxide Biology and Pathology, Academic Press, New York, 2000.
- [34] V. Tognido, R.S. da Silva, A.C. Tedesco, Inorg. Chim. Acta 316 (2001) 7, and references therein.
- [35] C.F. Fortney, S.J. Geib, F. Lin, R.E. Shepherd, Inorg. Chim. Acta 10 (2004) 2921.
- [36] E.A. Zuech, J. Chem. Soc., Chem. Commun. (1968) 1892.
- [37] E.A. Zuech, W.B. Hyghes, D.H. Kubicek, E.T. Kittleman, J. Am. Chem. Soc. 92 (1970) 528.
- [38] W.B. Hughes, Inorg. Chem. 13 (1974) 1531.
- [39] A. Keller, R. Matusiak, J. Mol. Cat. A: Chem. 142 (1999) 317.
- [40] D. Ballivet-Tkachenko, C. Bremard, F. Abraham, G. Nowogrocki, J. Chem. Soc. Dalton Trans. (1983) 1137.
- [41] M. Green, S.H. Taylor, J. Chem. Soc. Dalton Trans. (1973) 2629.
- [42] K. Bencze, J. Kohan, B. Mohai, L. Marko, J. Organomet. Chem. 70 (1974) 421.
- [43] S. Sarkar, P. Subramanian, Inorg. Chim. Acta 35 (1979) 357.
- [44] M.F. Perpinan, L. Ballester, A. Santos, A. Monge, C. Ruiz-Valero, E.G. Puebla, Polyhedron 6 (1987) 1523.
- [45] T.K. Banerjee, S.K. Brahma, S.P. Bag, Indian J. Chem. 30A (1991) 281.
- [46] R.C. Maurya, D.D. Mishra, S. Mukherjee, P.K. Trivedi, S.K. Jaiswal, Synth. React. Inorg. Met.-Org. Chem. 23 (1993) 723.
- [47] R.C. Maurya, D.D. Mishra, S. Mukherjee, S.K. Jaiswal, Synth. React. Inorg. Met.-Org. Chem. 23 (1993) 1073.
- [48] R.C. Maurya, D.D. Mishra, S. Mukherjee, S.K. Jaiswal, Synth. React. Inorg. Met.-Org. Chem. 24 (1994) 53.
- [49] R.C. Maurya, M.R. Maurya, S. Gopinathan, C. Gopinathan, Polyhedron 12 (1993) 159.
- [50] R.C. Maurya, D.D. Mishra, N.S. Rao, N.N. Rao, Polyhedron 13 (1994) 2653.
- [51] R.C. Maurya, A. Pandey, T. Singh, Synth. React. Inrog. Met.-Org. Chem. 32 (2002) 247.
- [52] B.S. Jensen, Acta Chim. Scand. 13 (1959) 1668.
- [53] R.C. Maurya, D.D. Mishra, N.S. Rao, N.N. Rao, Bull. Chem. Soc. Japan 68 (1995) 1592.
- [54] A.I. Vogel, Text book of Quantitative Inorganic Analysis, E.L.B.S, 1978, p. 471.
- [55] G. Svehla, Vogel's Qualitative Inorganic Analysis, sixth ed., Orient Longman Limited, UK, 1987, p. 163.
- [56] CS Chem 3D Ultra Molecular Modeling and Analysis, Cambridge; <www.cambridgesoft.com>.
- [57] R.C. Maurya, D.D. Mishra, N.S. Rao, M.N. Jayaswal, N.N. Rao, Polyhedron 12 (1993) 2045.
- [58] R.C. Maurya, T. Singh, B. Shukla, J. Dube, G.P. Shukla, Synth. React. Inorg. Met.-Org. Chem. 27 (1997) 1467.

- [59] R.C. Maurya, D.D. Mishra, S. Mukherjee, P.K. Trivedi, Transit. Metal Chem. 16 (1991) 524.
- [60] R.C. Maurya, D.D. Mishra, N.S. Rao, N.N. Rao, Shukla, Synth. React. Inorg. Met.-Org. Chem. 24 (1994) 1013.
- [61] R.C. Maurya, J. Dubey, B. Shukla, Synth. React. Inorg. Met.-Org. Chem. 28 (1998) 1159.
- [62] R.C. Maurya, V. Pillai, Indian J. Chem. 38A (1999) 736.
- [63] S. Sarkar, R.C. Maurya, S.C. Chaurasia, Transit. Metal Chem. 1 (1976) 49.
- [64] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [65] R.C. Maurya, S. Rajput, J. Mol. Struct. 687 (2004) 35.
- [66] R.C. Maurya, S. Rajput, J. Mol. Struct. (in press).