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Communications

Analysis of Trigonal-Prismatic and Octahedral Preferences in Hexaamine Cage Complexes

Sir:

Trigonal-prismatic stereochemistry (TP) was reported relatively early for extended lattices[1] and predicted for discrete molecules.[2] However, it was not until the mid-1960s with some surprise that the first structural characterization of a TP complex was received.[3] Since then various complexes with near-TP geometry have been reported[4] but for six-coordinate transition-metal complexes the octahedral (trigonal antiprismatic; TAP) geometry still predominates. We present here aspects of the structures of a series of complexes with varied metal centers (d^0–d^{10}) and a common sexidentate ligand (Figure 1). The series allows an analysis of the major influences, viz. preferred metal stereochemistry and the demands of the ligand, that dictate the compromise structures.

The hexaamine cage complexes[5] are not strictly axially symmetrical, but deviations from axial trigonal symmetry are minor perturbations.[6,7] The twist angles ϕ (the structural parameters are defined in Figure 1) cover a large range while other, not necessarily independent, structural parameters are roughly constant in all the structures ($b = 2.82 \pm 0.09$ Å; $s = 2.98 \pm 0.11$ Å; $\alpha = 82.2 \pm 2.5°$).[8] The metal–ligand bond lengths a are as expected from analogous transition-metal hexaamine complexes (see Table I), where available. It has to be pointed out that the substituents Y on the sar-type cage complexes do not have an important effect on the structure of the complexes. Most importantly, the effect on the twist angles ϕ seems to be negligible. This is clear from structural work[5b,c] and spectroscopic studies.[6]

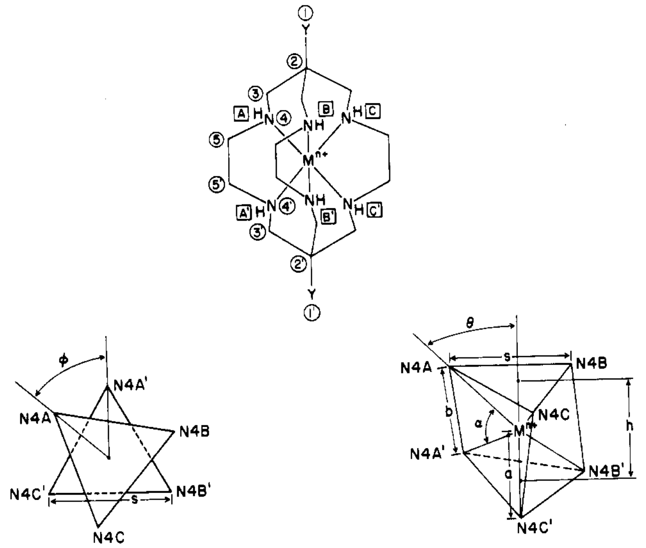

Figure 1. Structure, nomenclature, and numbering of the cage ligands (Y = H, sar; Y = NH_2, diamsar; Y = NH_3^+, di(amH)sar^{2+}, Y = NH_2OH^+, di(NH_2OH)sar^{2+}; 2 = N, sep) and definition of the structural parameters.

Figure 2 shows the twist angles ϕ in relation to the d-electron occupancy of the metal centers. There is a group of largely high-spin weak-ligand-field complexes whose structures are very close to that of the metal-free diprotonated ligand (**1**); i.e., the geometries are constant ($\phi \approx 28°$) and closer to the TP than the TAP limit. The twist angles ϕ of the other complexes (largely low spin and stronger ligand field) vary considerably between this structure and the TAP limit. The results can be rationalized by the expected differences in ligand field stabilization energies (ΔLFSE) for the two extreme structures (a qualitative energy level scheme is shown in Figure 3): on this basis there is little or no preference for either geometry for d^0, d^1, (low-spin d^2), high-spin d^5, high-spin d^6, and d^{10} systems; i.e., the ligand dictates the structure.[10] For all other electronic configurations a preference for TAP geometry exists that varies from a small preference for d^9 configurations and reaches a maximum with low-spin d^6.[11]

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(6) Comba, P., unpublished work.

(7) See Table I; distortions from trigonal symmetry are responsible for the fact that the twist angles ϕ are not well-defined in certain cases (error ≤7°). In addition, compressions and elongations along the pseudo trigonal axis[6] are not considered explicitly in this communication.

(8) The ligand structure is roughly constant with all CC– and CN– bonds and respective bond angles in the expected close range. There is only a small dependence of the parameters on the metal–ligand bond length a with the largest ions having the largest CC– and CN– bond lengths. Major exceptions are the vanadium complex, where throughout there are smaller CC– and CN– bonds, and the Co(II), Co(III), and Ni(II)[9] sepulchrate ions, where larger N4C3N2 and C3N2C3 angles and shorter N2C3 bonds obtain.[5b,c]

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(10) Although the ligand-dictated structure is clearly also a result of bonded and nonbonded interactions, we presume that the nonbonded interactions in the ligand framework provide the bias toward TAP geometry since there is no special strain introduced by the atom connectivity.

(11) In no instance can a preference for TP geometry be deduced solely from electronic factors (other similar[4b,12,13] and conceptually different models[14–16] reach similar conclusions). This explains partly the fact that the majority of hexacoordinate complexes are TAP.

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Table I. Structural Parameters[h]

complex	a, Å	b, Å	s, Å	s/h	α, deg	ϕ, deg	ref
di(amH)sar$H_2(NO_3)_4$ (**1**)		2.873 ± 0.159	3.043 ± 0.125	1.092		23.9 ± 7.2	*b*
Mg^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**2**)	2.188 ± 0.004	2.822 ± 0.002	2.984 ± 0.027	1.106	80.3 ± 0.1	27.8 ± 0.2	*b*
V^{IV}di(amH)sar-2H$(S_2O_6)_2{\cdot}2H_2O$ (**3**)	2.085 ± 0.016	2.644 ± 0.002	2.828 ± 0.011	1.090	78.7 ± 0.8	17.7 ± 0.05	*b*
Cr^{III}diamsar$Cl_3{\cdot}H_2O$ (**4**)	2.073 ± 0.006	2.777 ± 0.004	2.929 ± 0.013	1.222	84.1 ± 0.05	49.0 ± 0.7	*c*
Mn^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**5**)	2.238 ± 0.008	2.884 ± 0.020	3.053 ± 0.022	1.107	80.2 ± 0.6	27.6 ± 0.8	*b*
Fe^{III}sar$(NO_3)_3$ (**6**)	2.007 ± 0.021	2.719 ± 0.009	2.857 ± 0.019	1.247	85.2 ± 0.54	52.8 ± 0.9	*c*
Fe^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**7**)	2.202 ± 0.021	2.864 ± 0.021	2.979 ± 0.020	1.090	81.2 ± 0.5	28.6 ± 0.6	*b*
Co^{III}sep$(NO_3)_3$ (**8**)	1.974 ± 0.0	2.717 ± 0.0	2.818 ± 0.0	1.260	87.0 ± 0.0	56.7 ± 0.0	*d*
Co^{III}di(NH_2OH)sar$Cl_5{\cdot}4H_2O$ (**9**)	1.974 ± 0.005	2.730 ± 0.003	2.827 ± 0.008	1.273	87.5 ± 0.1	58.3 ± 0.4	*e*
Co^{II}sep$S_2O_6{\cdot}H_2O$ (**10**)	2.164 ± 0.011	2.831 ± 0.002	3.036 ± 0.018	1.200	81.9 ± 0.3	42.4 ± 0.8	*f*
Co^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**11**)	2.170 ± 0.021	2.830 ± 0.019	2.944 ± 0.031	1.091	81.4 ± 0.4	29.0 ± 0.9	*b*
Ni^{II}di(amH)sar$Cl_4{\cdot}H_2O$ (**12**)	2.111 ± 0.021	2.819 ± 0.017	2.963 ± 0.112	1.202	83.8 ± 1.0	45.7 ± 6.6	*b*
Ni^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**13**)	2.110 ± 0.008	2.816 ± 0.012	2.971 ± 0.023	1.207	83.8 ± 0.4	47.1 ± 1.1	*b*
Ni^{II}sep$(ClO_4)_2$ (**14**)	2.111 ± 0.005	2.790 ± 0.0	3.00 ± 0.0	1.247	82.7 ± 0.0	48.0 ± 0	*g*
Cu^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**15**)	2.169 ± 0.085	2.820 ± 0.030	2.965 ± 0.020	1.110	81.1 ± 1.6	29.8 ± 3.5	*b*
Ag^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**16**)	2.286 ± 0.077	2.953 ± 0.023	3.120 ± 0.039	1.111	80.4 ± 1.5	28.8 ± 2.5	*b*
Zn^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**17**)	2.190 ± 0.12	2.833 ± 0.016	2.933 ± 0.125	1.085	80.6 ± 0.4	28.6 ± 0.8	*b*
Cd^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**18**)	2.30 ± 0.028	2.966 ± 0.016	3.132 ± 0.038	1.103	80.4 ± 0.9	27.4 ± 0.8	*b*
Hg^{II}di(amH)sar$(NO_3)_4{\cdot}H_2O$ (**19**)	2.35 ± 0.029	3.006 ± 0.014	3.213 ± 0.027	1.112	79.5 ± 0.1	25.8 ± 1.0	*b*
mean (**2–19**)		2.823 ± 0.089	2.975 ± 0.108		82.2 ± 2.5		
octahedron (TAP)	a	$2^{1/2}a$	$2^{1/2}a$	$(3/7)^{1/2} = 1.22$	90	60	
trigonal prism (TP)[a]	a	$(3/7)^{1/2}2a$	$(3/7)^{1/2}2a$	1.0	81.8	0	

[a] The "regular" TP is assumed to have 1:1 faces.[20] [b] Reference 5b. [c] Reference 5c. [d] Geue, R. J.; et al., to be submitted for publication. [e] Balahura, R. J.; Ferguson, G.; Ruhl, B. L.; Wilkins, R. G. *Inorg. Chem.* **1983**, *22*, 3990. [f] Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016. [g] Reference 9. [h] For nomenclature see Figure 1. The mean and standard deviations are the result of three (ϕ, α, b, h) or six (a, s) independent parameters. The structural parameters have been calculated from atomic coordinates, which are from footnotes *b*–*g*.

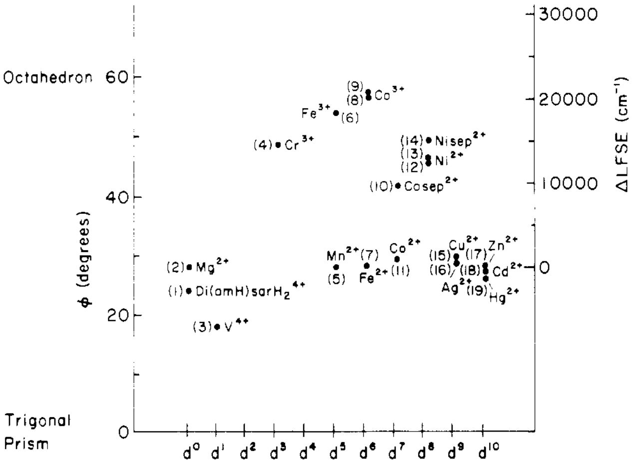

Figure 2. Twist angles ϕ as a function of the d-electron occupancy of the metal centers (for numbering see Table I). The ΔLFSE scale (cm^{-1}) is created by assuming two fixed points, viz. Mg(II) (**2**) and Cr(III) (**4**), and fitting their twist angles ϕ to the calculated difference ΔLFSE on the basis of the energy level scheme (Figure 3).

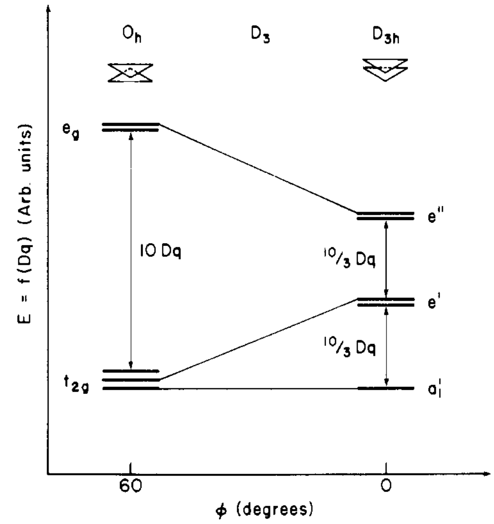

Figure 3. Qualitative energy level scheme for TAP and TP geometries.

With this simple qualitative ligand field model including differences in electron repulsion for the two extreme structures (TP and TAP), using the parameters from spectral studies[6,17] and assuming two fixed points (Mg(II) (**2**) and Cr(III) (**4**)), it is possible to estimate the twist angles ϕ within 5°.[6,18] This model is very simple and for the present purpose accurate enough in view of the variation of the experimental twist angles ϕ due to distortions from pure D_3 symmetry.

Clearly, the structures of the cage complexes and of compounds in general are the result of a compromise of inter- and intramolecular nonbonded interactions and electronic effects. Conclusions based solely on geometric[20–22] and/or repulsion[4c,21,24,25] models

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(17) The *Dq* values are in the expected range (~2000–2300 cm^{-1} for trivalent and ~1000–1300 cm^{-1} for divalent ions), and the Racah parameters *B* are, as expected, ≳50% of the parameters of the free ions.[6] Variations within these ranges give only small differences in the calculated twist angels ϕ. *Dq* values (cm^{-1}): Cr(III), 2235; Mn(II), 1182; Fe(III), 2002; Co(III), 2205; Co(II), 1157; Ni(II), 1242; Cu(II), 1086.

(18) Two data sets need special attention: (i) V^{IV}di(amH)sar-$2H^{4+}$ (in **3**) is deprotonated at two coordinated amine sites[19] and therefore not directly comparable with the other systems. Steric factors (smallest normalized bite b/a;[8] higher planarity of the coordinated amines[6]) and/or metal–ligand π bonding[14,16] may be responsible for the preference of TP geometry. (ii) $Co^{II}sep^{2+}$ (in **10**) again has a slightly different ligand system (in Co(III) and Ni(II) the difference seems to be unimportant since the structures there are relatively near the TAP limit). A larger side s resulting from a flatter cap (Table I)[8] may be responsible for the twist toward TAP geometry. The difference in *Dq* resulting from steric (smaller bond length a) and/or electronic (lone pair of the aza cap[6]) effects might also contribute.

(19) Neither X-ray data[5b] nor spectroscopy[6] is presently able to unequivocally locate the sites of deprotonation.

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are obviously only justifiable if complexes with metal centers of comparable electronic structures are involved. In our series, this would, for example, seem to be the case for systems with little or no preference for either TP or TAP structure (viz. d^0, d^1, (low-spin d^2), high-spin d^5, high-spin d^6, (d^9), and d^{10} on the basis of the ligand field model as outlined above) and the geometry is then the result of ligand dictation ($\phi \approx 28°$). For all other cases the electronic preferences cannot be neglected.[26]

Registry No. **1**, 96193-89-4; **2**, 96164-36-2; **3**, 96164-38-4; **4**, 96164-39-5; **5**, 96164-42-0; **6**, 96164-44-2; **7**, 96164-47-5; **8**, 88228-11-9; **9**, 96164-48-6; **10**, 96193-87-2; **11**, 72560-65-7; **12**, 96193-88-3; **13**, 96164-51-1; **14**, 88229-09-8; **15**, 96164-54-4; **16**, 92096-45-2; **17**, 96164-57-7; **18**, 96164-60-2; **19**, 96164-63-5.

Research School of Chemistry
Australian National University
Canberra, ACT 2601, Australia
Peter Comba*[27]
Alan M. Sargeson

Department of Physical and Inorganic Chemistry
University of Western Australia
Nedlands, WA 6009, Australia
Lutz M. Engelhardt
Jack MacB. Harrowfield
Allan H. White

Department of Physical and Inorganic Chemistry
University of Adelaide
Adelaide, SA 5001, Australia
Ernst Horn
Michael R. Snow

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(26) $M(en)_3^{n+}$ complexes, for example, show the same general trends[6] although the range of the twist angles ϕ is much smaller (~49-54°).

(27) To whom correspondence should be addressed at Université de Lausanne, Institut de Chimie Minérale et Analytique, 1005 Lausanne, Switzerland.

Articles

Contribution No. 858 from the Battelle-C. F. Kettering Research Laboratory,
Yellow Springs, Ohio 45387

Synthetic Utility of Molybdenum–Diazene Adducts: Preparation, Reactions, and Spectral Properties of Oxo-Free and (^{18}O)Oxo Molybdenum Complexes

GRACE J.-J. CHEN, JOHN W. McDONALD,* DUDLEY C. BRAVARD, and W. E. NEWTON*

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Compounds of the type $Mo(LL)_2(DEAZ)_x$ (LL = S_2CNR_2, $S_2P(i\text{-}Pr)_2$, $S_2P(OEt)_2$; DEAZ = diethyl diazenedicarboxylate; x = 1, 2) are prepared from $Mo(CO)_2(LL)_2$. Their facile protonation by water and other reagents ($o\text{-}C_6H_4(XH)_2$: $X_2 = S_2$; O_2; S, O; S, NH; S, NMe) to release the hydrazine ($DEAZH_2$) has been used to prepare oxo-free and oxo-containing species. $o\text{-}C_6H_4(XH)_2$ and HOC_2H_4SH react with $Mo(S_2CNEt_2)_2(DEAZ)$ to produce $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4X_2)$ or $Mo(S_2CNEt_2)_2(OC_2H_4S)$. Some of these same compounds can be produced by oxo removal by these same reagents from $OMo(S_2CNEt_2)_2$. Some of these products can be oxidized to Mo(V) and Mo(VI) compounds by Cl_2 and O_2 to give $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4X_2)$ ($X_2 = S_2$; O, S; S, NMe) and $OMo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$, respectively. Hydrolysis of $Mo(S_2CNR_2)_2(DEAZ)_2$ produces $MoO_2(S_2CNR_2)_2$ and $DEAZH_2$. Hydrolysis of a reaction mixture containing $Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$ and DEAZ gives a mixture of $MoO_2[S_2P(i\text{-}Pr)_2]_2$ and $Mo_2O_4[S_2P(i\text{-}Pr)_2]_2$, while $Mo(CO)_2(PPh_3)[S_2P(OEt)_2]_2$ and DEAZ, after hydrolysis, give some $Mo_2O_3[S_2P(OEt)_2]_4$. Complexes of stoichiometry $Mo^{18}O_2(LL)_2$, $Mo^{18}O(LL)_2$, $Mo_2{}^{18}O_3(LL)_4$, $Mo_2{}^{18}O_4(LL)_2$, and $Mo_2{}^{18}O_3S(LL)_2$ (LL = S_2CNR_2, $S_2P(OR)_2$, S_2PR_2; not all compounds were formed with each ligand) are produced by the reaction series (i) controlled hydrolysis with $H_2{}^{18}O$ of diazene adducts, $Mo(LL)_2(DEAZ)_2$, and (ii) reduction of $Mo^{18}O_2(LL)_2$ with tertiary phosphine. Reaction of $Mo_2O_4(LL)_2$ with H_2S gives $Mo_2O_3S(LL)_2$. By spectral comparisons with their ^{16}O analogues, definitive unambiguous assignments of both terminal and bridging molybdenum–oxygen stretching vibrations are made.

Introduction

There has been considerable recent interest in diazene complexes of transition metals,[1] particularly because of their potential involvement as intermediates in the catalyzed (both chemical and enzymic) reduction of dinitrogen to ammonia.[2-4] We have been particularly interested in molybdenum complexes of these moieties and have previously described the catalytic reduction of diazenes by the Mo(IV) species $OMo(S_2CNR_2)_2$, the crystal and molecular structure of $OMo(S_2CNMe_2)_2(C_6H_5CON_2COC_6H_5)$, and the possible relevance of the hydrolysis of the complexes $OMo(S_2CNR_2)_2(diazene)$ to that displayed by molybdoenzymes (eq 1).[2,5,6] The preparation of[7,8] the compounds $Mo(S_2CNR_2)_2$-

$$OMo(S_2CNR_2)_2(RN_2R) + H_2O \rightarrow MoO_2(S_2CNR_2)_2 + RHN_2HR \quad (1)$$

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(1) See, for example: Ittel, S. D.; Ibers, J. A. *Inorg. Chem.* **1970**, *14*, 1183. Dickson, R. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2988. Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108. Bailey, N. A.; Frisch, P. D.; McCleverty, J. A.; Walker, N. W.; Williams, J. *J. Chem. Soc., Chem. Commun.* **1975**, 350. Carroll, J. A.; Sutton, D.; Cowie, M.; Gauthier, M. D. *J. Chem. Soc., Chem. Commun.* **1979**, 1058. Chatt, J.; Dilworth, J. R.; Dahlstrom, P. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 786. Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 914. Butcher, A. V.; Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 921. Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 279. Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1603.

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