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Preparation and Circular Dichroism Spectrum of the Tetrakis(*R*-1,2-diaminopropane)dimolybdenum Cation: Evidence for a Bridged Structure

Sir:

There is only one report of a dimolybdenum complex containing unsaturated diamine ligands— $[\text{Mo}_2(\text{en})_4]^{4+}$ —and even that compound has not been structurally characterized.¹ Bowen and Taube suggested,¹ from an inspection of scale models, that $[\text{Mo}_2(\text{en})_4]^{4+}$ was more likely to contain chelating than bridging diamine ligands (Figure 1). We have recently shown² for complexes of dimolybdenum containing bidentate bis(diphenylphosphino) ligands, such as dppe, that the bridged isomer is thermodynamically more stable than the chelated isomer and that the latter spontaneously isomerizes in dry methylene chloride solution. We wish to report here the synthesis and CD spectrum of $[\text{Mo}_2(\text{R-pn})_4]^{4+}$, the first chiral dimolybdenum complex containing diamine ligands, and conclude from the CD spectrum that the complex must have a staggered configuration and thus bridging ligands.

The complex was synthesized by the method described by Bowen and Taube for the ethylenediamine analogue¹ and gave satisfactory analysis. The absorption and CD spectra of the chloride salt in 0.1 M HCl are shown in Figure 2. The absorption spectrum is very similar to that of $[\text{Mo}_2(\text{en})_4]^{4+}$, the major difference being a blue shift and intensification of the $\delta \rightarrow \delta^*$ transition in the *R*-pn complex. The CD spectrum of $[\text{Mo}_2(\text{R-pn})_4]^{4+}$ bears a close similarity (apart from the absolute wavelengths of the transitions) to that of the structurally characterized complex $\text{Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$, which contains bridging diphosphine ligands and a staggered $\text{Mo}_2\text{Cl}_4\text{P}_4$ chromophore. In both complexes large Cotton effects are observed under both the $\delta \rightarrow \delta^*$ transition and under the next highest energy absorption (which is assigned as a magnetic dipole transition). The dissymmetry factors ($\Delta\epsilon/\epsilon$) are similar for the two compounds and are typical for configurationally chiral metal complexes. Indeed, the dissymmetry factor for the magnetic dipole transition of $[\text{Mo}_2(\text{R-pn})_4]^{4+}$ (17×10^{-2}) is among the largest recorded for a solution spectrum of an inorganic compound and is comparable with those found for single-crystal CD spectra of configurationally chiral metal complexes (for example the ${}^1\text{A}_1 \rightarrow {}^1\text{E}$ transition of $\Delta\text{-Co}(\text{en})_3\text{Cl}_3$ has $\Delta\epsilon/\epsilon = 22 \times 10^{-2}$).

We have also prepared both the chelated (α) and bridged (β) isomers of $\text{Mo}_2\text{Cl}_4(\text{R-dppp})_2$ and obtained their CD spectra. As expected, the bridged isomer has a CD spectrum of magnitude similar (but with inversion of sign) to that of $\text{Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ (the dissymmetry factor of the $\delta \rightarrow \delta^*$ transition is 6×10^{-3}). The chelated isomer, in which the two MoCl_2P_2 units are eclipsed, has on the other hand such a weak optical activity that we could detect no CD spectrum (implying $\Delta\epsilon/\epsilon < 5 \times 10^{-5}$). Thus the presence of a chiral center on the ligand backbone is not in itself sufficient to produce a significant Cotton effect under the $\delta \rightarrow \delta^*$ transition and the observation of such an effect must therefore imply a staggered chromophore. Both the magnitude of the CD spectrum

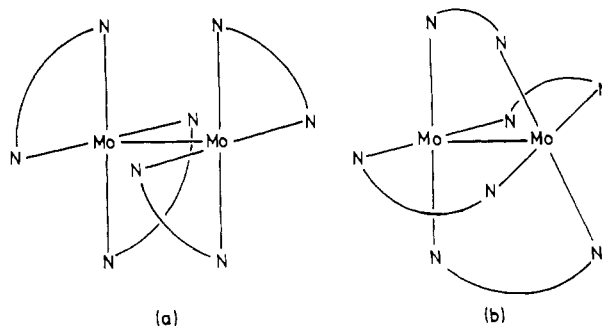


Figure 1. Schematic representation of the isomers of $[\text{Mo}_2(\text{en})_4]^{4+}$: (a) chelated (α) isomer; (b) bridged (β) isomer.

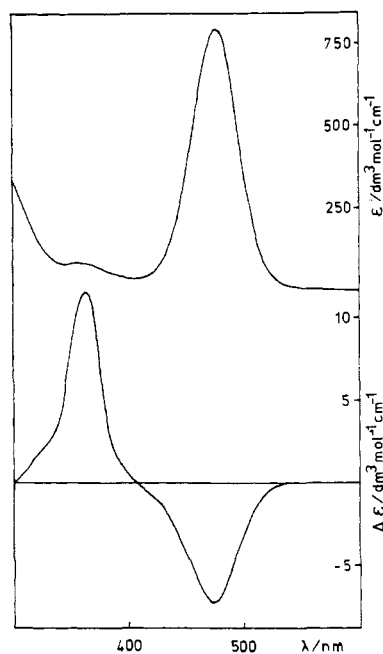


Figure 2. Absorption and CD spectra of a solution ($10^{-3} \text{ mol L}^{-1}$) of $[\text{Mo}_2(\text{R-pn})_4]^{4+}$ as the chloride salt in $10^{-2} \text{ mol L}^{-1}$ HCl.

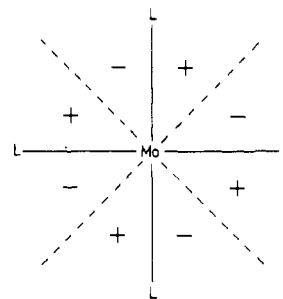


Figure 3. Sector rule for the sign of the CD under the $\delta \rightarrow \delta^*$ transition of $[\text{Mo}_2(\text{L L})_4]^{4+}$. The sign of the CD is that of the sectors containing the L atoms of the rear MoL_4 or $\text{MoL}_2\text{L}'_2$ unit.

of $[\text{Mo}_2(\text{R-pn})_4]^{4+}$ and its qualitative similarity to those of the β isomers of the diphosphine complexes lead to the conclusion that the complex contains a staggered Mo_2N_8 chromophore. Although it is just possible that chelating diamine ligands could result in a staggered stereochemistry about the Mo-Mo bond, the evidence from complexes with diphosphine and dithiol ligands is that a staggered geometry is produced only by the conformational preference of bridging ligands. We conclude, therefore, that $[\text{Mo}_2(\text{R-pn})_4]^{4+}$ contains bridging diamine ligands. The close similarity of the absorption spectra as well as the similar preparative methods make it extremely likely that $[\text{Mo}_2(\text{en})_4]^{4+}$ also has a bridged structure.

The simple metal-localized model for the CD of the $\delta \rightarrow \delta^*$ transition described in ref 3 leads to a sector rule relating the twist

(1) Bowen, A. R.; Taube, H. *Inorg. Chem.* 1974, 13, 2245-2249.
(2) Fraser, I. F.; McVitie, A.; Peacock, R. D. *J. Chem. Res., Synop.* 1984, 420-421.

of the two MoL_4 (or $\text{MoL}_2\text{L}'_2$) units to the sign of the CD band. This is summarized in Figure 3. The sector rule predicts that $\text{Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ should have either the Λ configuration⁴ with a twist angle of between 0 and 45° or the Δ configuration with a twist angle between 45 and 90°. Since the conformational preference of the $\text{Mo}_2\text{P}_2\text{C}_2$ rings (dictated by the S configuration of the methyl groups) is expected to impose the Λ configuration on the complex, the sector rule predicts that the twist angle of the two MoP_2Cl_2 units should be less than 45°. This has been confirmed by crystallography:⁵ $\text{Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ has the Λ configuration and a twist angle of 23°. The Cotton effect shown by the $\delta \rightarrow \delta^*$ transition of $\beta\text{-Mo}_2\text{Cl}_4(\text{R-dppp})_2$ implies (given the Δ configuration dictated by the R conformation of the methyl group) that this complex also has a twist angle of less than 45°. The CD spectrum of the $\delta \rightarrow \delta^*$ transition of $[\text{Mo}_2(\text{R-pn})_4]^{4+}$ has the sign opposite to that found for $\beta\text{-Mo}_2\text{Cl}_4(\text{R-dppp})_2$. Since the R conformation of the methyl groups will impose the same (Δ) configuration on both complexes, we conclude that the twist between the two MoN_4 units of $[\text{Mo}_2(\text{R-pn})_4]^{4+}$ is between 45 and 90°, in contrast to that for the diphosphine complexes. The CD spectrum of $[\text{Mo}_2(\text{S,S,-bn})_4]^{4+}$ has, as expected, a magnitude similar and sign opposite to that of the $R\text{-pn}$ complex, implying once again a twist of greater than 45°.

Acknowledgment. We thank the U.K. Science and Engineering Research Council for a studentship (I.F.F.)

- (3) Agaskar, P. A.; Cotton, F. A.; Fraser, I. F.; Peacock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1851-1853.
- (4) The absolute configuration is given by the twist of the two MoL_4 or $\text{MoL}_2\text{L}'_2$ units about the Mo-Mo bond. If, as one looks down the Mo-Mo bond, the rear MoL_4 unit is rotated counterclockwise, the complex has the Λ configuration and vice versa.
- (5) Agaskar, P. A.; Cotton, F. A.; Fraser, I. F.; Manojlovic-Muir, Lj.; Muir, K.; Peacock, R. D., paper in preparation.

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Chemistry of Mono(guanine) Complexes of Cisplatin and Its Relevance to the N7,O6 Chelate Hypothesis

Sir:

Of all the theories put forward to explain the antitumor activity of $\text{cis}-(\text{NH}_3)_2\text{PtCl}_2$ (cisplatin) and the inactivity of the *trans* isomer, the so-called N7,O6 chelate hypothesis has evoked the biggest controversy.¹ In brief, this hypothesis assumes the formation of a specific cross-link of $\text{cis}-(\text{NH}_3)_2\text{Pt}^{\text{II}}$ with the nucleobase guanine through N7 and O6, which would then affect the normal hydrogen-bonding pattern of guanine and lead to base-substitution mutations and eventually to cell death.² *trans*-(NH_3)₂Pt^{II} is not capable of forming such a chelate.

Our approach to the question of chelate formation of $\text{cis}-(\text{NH}_3)_2\text{Pt}^{\text{II}}$ with guanine was as follows: By replacement of the chloro ligand in $\text{cis}-(\text{NH}_3)_2\text{Pt}(\text{G-N}^7)\text{Cl}^+$ (G = 9-ethylguanine, platinated at N7),³ with the aqua ligand (Figure 1), the behavior of the aqua diammine 9-ethylguanine complex 1 was studied.⁴ It

- (1) For a critical evaluation see, e.g.: (a) Chu, G. Y. H.; Mansy, S.; Duncan, R. E.; Tobias, R. S. *J. Am. Chem. Soc.* **1978**, *100*, 593. (b) Martin, R. B.; Mariam Y. H. *Met. Ions Biol. Syst.* **1979**, *8*, 55.
- (2) Rosenberg, B. *Biochimie* **1978**, *60*, 859 and references cited therein.
- (3) Raudaschl, G.; Lippert, B. *Inorg. Chim. Acta* **1983**, *80*, L 49.
- (4) Preparation of 1: A 0.1-mmol sample of $\text{cis}-(\text{NH}_3)_2\text{Pt}(\text{G})\text{Cl}^+\text{Cl}^- \cdot 0.5\text{H}_2\text{O}$ is suspended in 1 mL of D_2O , and 0.2 mmol of AgNO_3 is added. The slurry is stirred at 0-3 °C for 6 h and then centrifuged from AgCl : colorless solution, pD 2.5.

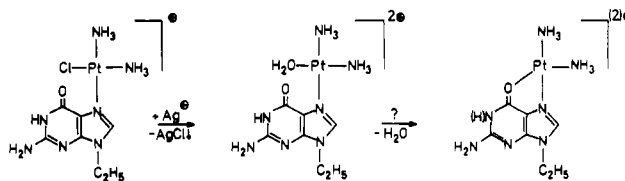


Figure 1. Formation of $\text{cis}-(\text{NH}_3)_2\text{Pt}(\text{G})\text{H}_2\text{O}^{2+}$ (1).

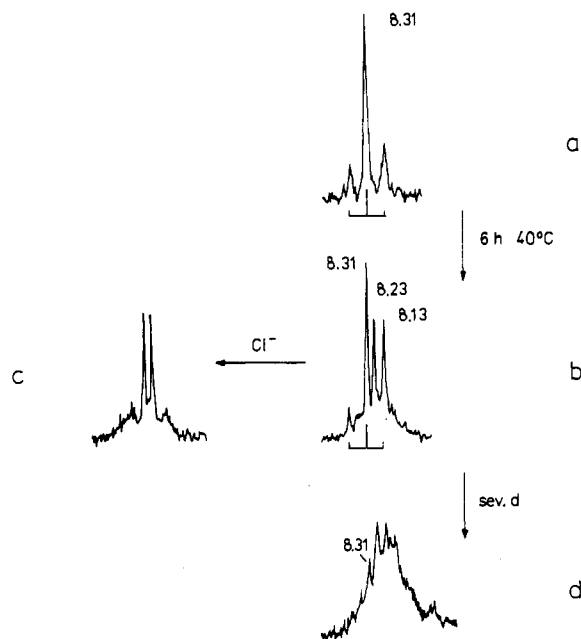


Figure 2. ¹H NMR spectra (H8 resonances only, D_2O , 0.1 M Pt) of $\text{cis}-(\text{NH}_3)_2\text{Pt}(\text{G})\text{D}_2\text{O}^{2+}$ (1) prepared as described in ref 4: (a) at pD 2.5; (b) at pD 1.8, 6 h at 40 °C after spectrum a; (c) after addition of 30 mg of NaCl and centrifugation of precipitated $\text{cis}-(\text{NH}_3)_2\text{Pt}(\text{G})\text{Cl}^+\text{Cl}^-$ (1'); (d) without addition of NaCl, 4 days at 22 °C after spectrum b at pD 1.6. Internal reference in all cases was $[\text{NMe}_4]^+$.

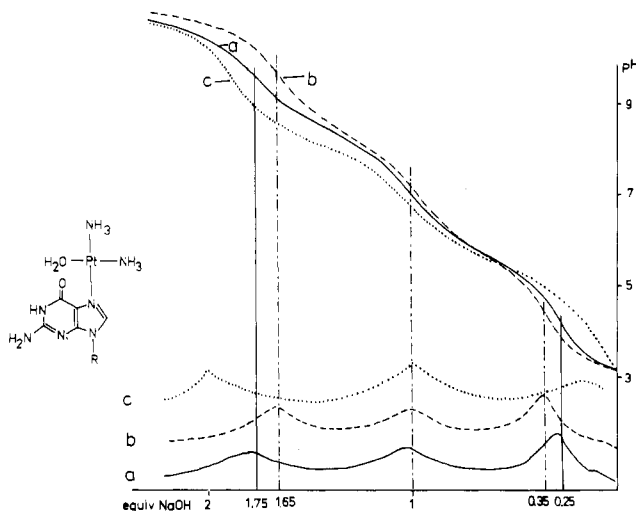


Figure 3. Titration curves (top) and derivatives (bottom): (a) of aged $\text{cis}-(\text{NH}_3)_2\text{Pt}(\text{G})\text{H}_2\text{O}^{2+}$ (1 h at 22 °C after preparation according to ref 4 and then diluted as described in ref 6); (b) of aged $\text{cis}-(\text{NH}_3)_2\text{Pt}(\text{G})\text{H}_2\text{O}^{2+}$ (20 min at 80 °C and 2 h at 22 °C); (c) under the assumption that 1 remains unchanged.

was assumed that if chelate formation were to take place, it should occur from precursor 1.

Figure 2 gives the ¹H NMR spectroscopic changes of 1 with time. As can be seen, the spectrum changes rapidly, and in an early stage of the reaction, two new sets of resonances in exactly 1:1 ratio are formed. The reaction can be stopped at this point by adding an excess of NaCl,⁵ which precipitates unreacted 1 as