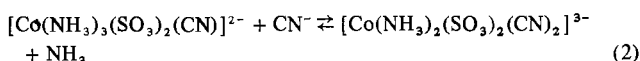
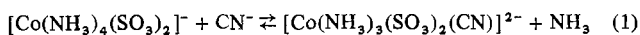


To further characterize the labilizing influence of sulfito ligands similar $^{15}\text{NH}_3$ exchange experiments were performed on the complex $[\text{cis-Co}(\text{NH}_3)_4(\text{SO}_3)_2]^-$. The results, also summarized in Table I, reveal that in this case *two* (1.94 ± 0.2) NH_3 ligands exchange with $^{15}\text{NH}_3$, the product presumably being $[(\text{trans-NH}_3)_2(\text{cis-}^{15}\text{NH}_3)_2(\text{cis-SO}_3)_2\text{-Co}]^-$. This result confirms the specific trans-labilizing effect of the sulfito ligand and further demonstrates the essential independence of this effect for each sulfito ligand when two such ligands are present in the same complex.

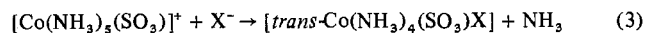
Control $^{15}\text{NH}_3$ -exchange experiments were performed on $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{S}_2\text{O}_3)]^+$. Each complex was allowed to react with excess aqueous $^{15}\text{NH}_3$ (49% enrichment) for several hours. Samples of the thiosulfato complex contained 0.6% ^{15}N after 0.5 h of reaction, 0.9% ^{15}N after 2.5 h, 1.1% after 5 h, 1.5% after 15 h, and 1.8% after 26 h. One sample of the nitrite complex reaction contained 0.9% ^{15}N after 26 h of reaction. After 26 h, decomposition of the complex was observed in both cases.

The results indicate that fewer than 0.2 of the 5 NH_3 ligands were exchanging with $^{15}\text{NH}_3$ after 26 h of reaction and demonstrate that, in contrast to the sulfito ligand, the nitrite and thiosulfato ligands do not exert strong trans-labilizing influences on $\text{Co}(\text{III})$ complexes.

As expected, the presence of two SO_3^{2-} ligands in $[\text{cis-Co}(\text{NH}_3)_4(\text{SO}_3)_2]^-$ also gave rise to facile substitution of two NH_3 ligands by other ligands, for example CN^- , SO_3^{2-} , and NCS^- . In each case two distinct consecutive substitution reactions could be identified spectrophotometrically,¹² as the concentration of the substituting anion was increased, for example

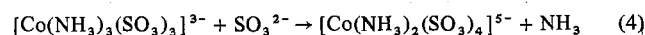


Preliminary kinetic measurements at 25 °C yielded a limiting first-order rate law, i.e., $k[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]^-$, for reaction 1, as well as for the corresponding reactions with SCN^- and SO_3^{2-} . In each case the rate of reaction was independent of the concentration of the substituting anion (for example, over the concentration range 0.01–0.05 M, in the case of CN^-), and in each case the value of k was found to be $0.15 \pm 0.02 \text{ s}^{-1}$. This kinetic behavior is consistent with, but does not unequivocally demonstrate, a dissociative mechanism similar to that proposed for related substitution reactions of $[\text{Co}(\text{NH}_3)_5(\text{SO}_3)]^+$ and $[\text{trans-Co}(\text{CN})_4(\text{SO}_3)(\text{H}_2\text{O})]^{3-}$. The value $k = 0.15 \text{ s}^{-1}$ compares with a value of 0.012 s^{-1} for the corresponding limiting first-order rate constants for the substitution reactions of $[\text{Co}(\text{NH}_3)_5(\text{SO}_3)]^+$ with various ligands, i.e.



where $\text{X}^- = \text{OH}^-$, CN^- , NO_2^- , or SCN^- . The effect of introducing a second SO_3^{2-} ligand into the complex (i.e., in a *cis* position to the NH_3 ligand undergoing replacement) is, thus, to enhance the lability of the complex, but only by a factor of about 12 which seems surprisingly small, especially in view of the change in charge on going from $[\text{Co}(\text{NH}_3)_5(\text{SO}_3)]^+$ to $[\text{cis-Co}(\text{NH}_3)_4(\text{SO}_3)_2]^-$.

Introduction of a third sulfito ligand was accompanied by only a very slight further enhancement of lability, as reflected in a value of $0.22 \pm 0.03 \text{ s}^{-1}$ for the limiting first-order rate constant (invariant over the concentration ranges 0.01–0.02 M NH_3 and 0.25–0.35 M SO_3^{2-}) for the reaction



These comparisons serve to emphasize the strikingly specific trans-labilizing influence of each SO_3^{2-} ligand (and apparent

absence of accompanying *cis* influences) even when several such ligands are present in the same cobalt(III) complex. The origin of this remarkable influence remains to be fully elucidated.

Acknowledgment. Support of this research through grants from the National Science Foundation and National Institutes of Health is gratefully acknowledged.

Registry No. 1, 59753-02-5; 2, 53165-58-5; $[\text{Co}(\text{NH}_3)_4(^{15}\text{N-H}_3)(\text{SO}_3)_2]\text{SO}_3$, 59753-04-7; $\text{NH}_4[\text{cis-Co}(\text{NH}_3)_2(^{15}\text{NH}_3)_2(\text{SO}_3)_2]$, 59753-05-8.

References and Notes

- (1) To whom correspondence should be addressed.
- (2) J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta, Rev.*, **5**, 7 (1971), and references therein.
- (3) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Am. Chem. Soc.*, **88**, 2877 (1966).
- (4) J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).
- (5) A. V. Babaeva and I. B. Baranovskii, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **7**, 404 (1962).
- (6) P. H. Tewari, R. W. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967).
- (7) H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.*, **7**, 2535 (1968).
- (8) R. Klement, *Z. Anorg. Allg. Chem.*, **150**, 117 (1925).
- (9) The result of this study has been reported in a preliminary communication³ and subsequently confirmed.¹¹ Experimental details of our original work are provided in the present paper.
- (10) A. Werner and H. Gruger, *Z. Anorg. Allg. Chem.*, **16**, 399 (1898).
- (11) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5129 (1967).
- (12) For example: for $[\text{cis-Co}(\text{NH}_3)_4(\text{SO}_3)_2]^-$, λ_{max} 454 nm (ϵ $2.1 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$); for $[\text{Co}(\text{NH}_3)_3(\text{SO}_3)_2(\text{CN})]$, λ_{max} 425 nm (ϵ 2.0×10^2); for $[\text{Co}(\text{NH}_3)_2(\text{SO}_3)_2(\text{CN})_2]^-$, λ_{sh} 421 nm (ϵ 1.66×10^2). The compositions of the products of reactions 1, 2, and 4 were confirmed by spectral titrations.

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

Structure of 1,6-Dioxo-4,9-diaza-5 λ^5 -phosphaspiro[4.4]nonane, $(\text{OCH}_2\text{CH}_2\text{NH})_2\text{PH}$, by X-Ray Diffraction and Computer Simulation

Paul F. Meunier, Joan A. Deiters, and Robert R. Holmes*

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In the context of the Gillespie-Nyholm electron pair repulsion theory (VSEPR),¹ it is of some importance to establish if a small atom like hydrogen, equatorially bonded to phosphorus in a trigonal-bipyramidal framework, is capable of exerting a greater repulsion effect than larger more electronegative atoms positioned at similar equatorial sites. The only substance so far investigated for which an equatorial P–H bond is indicated is HPF_4 whose P–H bond distance was assumed in a structural analysis of its microwave rotational spectrum.² The $F_{\text{ap}}\text{-P-H}_{\text{eq}}$ angle was reported² as $90 \pm 4^\circ$. By way of contrast, x-ray analysis³ of the interesting tricyclophosphorane $[\text{HP}(\text{OCH}_2\text{CH}_2)_3\text{N}]\text{BF}_4$ revealed an apical P–H bond in a trigonal-bipyramidal frame containing an internal P←N dative bond.

An x-ray diffraction study⁴ of the highly substituted spirophosphorane I showed the apical oxygen atoms tilted

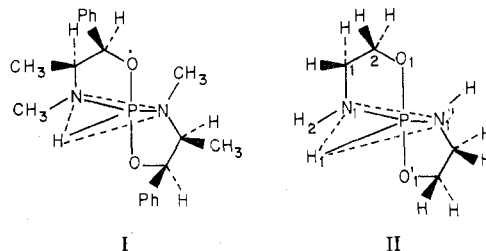


Table I. Bond Lengths (Å) and Bond Angles (deg) for II^a

Bond Lengths					
	X-ray	Calcd		X-ray	Calcd
P-O ₁	1.709 (2)	1.70	N ₁ -C ₁	1.448 (5)	1.45
P-N ₁	1.671 (3)	1.67	C ₁ -C ₂	1.518 (5)	1.51
P-H ₁	1.47 (6)	1.46	N ₁ -H ₂	0.82 (4)	
O ₁ -C ₂	1.441 (4)	1.44			
Bond Angles					
	X-ray	Calcd ^c		X-ray	Calcd ^c
O ₁ -P-O ₁ '	177.0 (1) ^b	179.1 ^d	P-O ₁ -C ₂	111.6 (2)	112.1
N ₁ -P-N ₁ '	131.7 (1)	127.0	P-N ₁ -C ₁	119.6 (2)	116.7
H ₁ -P-N ₁ '	114.1 (12)	116.5	P-N ₁ -H ₂	121.0 (29)	124.3
H ₁ -P-O ₁	91.5 (12)	89.5	C ₁ -N ₁ -H ₂	118.9 (29)	119.0
O ₁ -P-N ₁ '	88.2 (1)	90.4	O ₁ -C ₂ -C ₁	107.2 (3)	106.7
O ₁ -P-N ₁ '	90.5 (1)	90.0	N ₁ -C ₁ -C ₂	102.0 (3)	104.0

^a The esd's are shown in parentheses. Refer to II for the numbering scheme. ^b The apical PO bonds are bent away from the equatorial P-H linkage. ^c See ref 7. ^d The apical PO bonds are deflected 0.5° each toward the equatorial P-H bond. However, the approximate nature of the calculations at this stage, angles reproducible to ±2°, does not make the direction of tilting meaningful.

slightly toward an equatorially oriented hydrogen atom. However, refinement of hydrogen atom positions was not successful.

In an attempt to clarify the role of the directly bonded hydrogen atom, we have carried out the x-ray structural determination of a spirophosphorane analogous to I, but containing no substituents other than hydrogen atoms on the ring carbons, thereby maintaining intramolecular interactions at a minimum. Elucidation of the structure of this spirophosphorane II allowed the P-H bond distance to refine. Furthermore, computer simulation by conformational energy minimization accurately reproduces most features of the phosphorane structure.

Crystals (colorless, 0.9 × 0.05 × 0.05 mm, needle axis (c) aligned parallel to φ axis of goniometer) of II prepared as described by Burgada⁵ are monoclinic, of space group C2/c, with *a* = 10.16 Å, *b* = 7.78 Å, *c* = 10.44 Å, β = 120.50°, *V* = 714.7 Å³, *d*_{calcd} = 1.39 g cm⁻³, and *Z* = 4. The molecules contain a crystallographic twofold axis lying along the P-H bond. Consistent with the space group C2/c, the systematic absences were *hkl*, *h* + *k* = 2*n* + 1, and *h0l*, *l* = 2*n* + 1.

Intensity data were collected with an Enraf-Nonius CAD-3 diffractometer using Zr-filtered, Mo Kα radiation. With anisotropic temperature factors for the phosphorus, oxygen, nitrogen, and carbon atoms and isotropic refinement of the hydrogen atom positions, the *R* value converged to 0.062 for 477 observed unique reflections (*I* > 2σ(*I*)). Bond distances and bond angles are given in Table I and an ORTEP plot⁶ of the molecular geometry is presented in Figure 1. Also included in Table I is a comparison of x-ray and calculated bond parameters based on a conformational energy minimization scheme.⁷

The structural data for II reveal modest distortions from a trigonal bipyramid. The most striking departure is the opening of the N₁-P-N₁' angle to 131.7°. In CH₃PF₄,⁸ for example, the F-P-F equatorial angle closes to 115.6° in agreement with the greater electron pair repulsion exerted by the P-C bond compared to the P-F bonds. It is noted as an important feature of the present study that the apical oxygen atoms are tilted away from the equatorial P-H bond in accord with VSEPR theory.¹ However, the presence of apical and equatorial atoms linked by ring constraints is a new feature and may be important in influencing the observed direction of tilt.

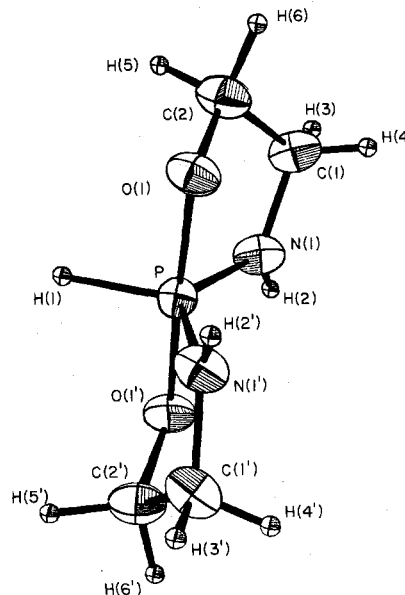


Figure 1. Molecular geometry of (OCH₂CH₂NH)₂PH. Thermal ellipsoids are drawn at the 50% probability level.

We find that intermolecular hydrogen bonding, as evidenced by the N-H...O distance of 3.05 Å, adequately accounts for the observed N₁-P-N₁' angle. Inclusion of this term in the computer minimization program yields a calculated angle of 127°, still somewhat lower than the observed value of 131.7°, but considerably greater than the computed value of 117.6° obtained without the presence of this term. The conformational calculation includes an electron pair repulsion effect for atoms around phosphorus. Apparently, the effects of ring constraints are not sufficient to cause any widening of the N-P-N angle over the regular angle of 120° in our program. This point, however, is subject to further investigation.

The widening of the N₁-P-N₁' angle in II compares with a similar observation in the related structure (OCH₂-C(CH₃)₂NH)₂PH. Preliminary x-ray data⁹ reveal an angle of about 127°. Again intermolecular N-H...O hydrogen bonding appears in the crystal-packing arrangement with N...O distances of ~3.2 Å.⁹ Furthermore, the presence of coplanarity of nitrogen and the attached atoms in I⁴ and II suggests a degree of π back-bonding between nitrogen filled p orbitals and phosphorus vacant d orbitals. From theoretical considerations,¹⁰ the π bond is expected to concentrate in the equatorial plane. Thus, the N-P-N angle should widen from 120° on this basis as well. In I, where no hydrogen bonding is possible, the N-P-N angle is 123°. Accordingly, we conclude that the spirophosphorane structure II is consistent with the VSEPR theory, the widening of the equatorial N₁-P-N₁' angle being determined by a combination of intermolecular hydrogen bonding and equatorial in-plane electron pair repulsion, where both σ- and π-electron density contributes, and the tilting of the axial oxygen atoms away from the equatorial P-H bond reflecting the effect of electron density concentrated toward the phosphorus atom in the P-H bond.

Analogous to the case of I, ring puckering in II takes place at the O-C₂-C₁ angle but in an opposite direction. In II the flap atom C₂ is displaced toward the P-H equatorial bond. The ring puckering effect in II has been observed in an NMR study,¹¹ a result of which suggests a low torsional barrier to inversion at the flap atom C₂. The conformational calculation indicates that the opposite puckering in I is primarily associated with atom-atom repulsions brought about by the presence of the large phenyl groups in place of protons that reside in II. As in I,⁴ the nitrogen and attached atoms in II are coplanar.

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Registry No. (OCH₂CH₂NH)₂PH, 1491-22-1.

References and Notes

- (1) R. J. Gillespie and R. S. Nyholm, *Q. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); *J. Chem. Educ.*, **40**, 295 (1963).
- (2) S. B. Pierce and C. D. Cornwell, *J. Chem. Phys.*, **48**, 2118 (1968).
- (3) J. C. Clardy, D. S. Milbrath, J. P. Springer, and J. G. Verkade, *J. Am. Chem. Soc.*, **98**, 623 (1976).
- (4) M. G. Newton, J. E. Collier, and R. Wolf, *J. Am. Chem. Soc.*, **96**, 6888 (1974).
- (5) R. Burgada, *Ann. Chim. (Paris)*, **8**, 347 (1963).
- (6) C. K. Johnson's program ORTEP: Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
- (7) The Fortran program MMI, by Allinger, was modified for a CDC computer and changed to (1) treat five-coordinate atoms and (2) calculate electron pair repulsion terms between atoms bound to phosphorus. For a description of Allinger's program, see N. L. Allinger et al., *J. Am. Chem. Soc.*, **93**, 1637 (1971). A complete discussion of the application of the modified program to phosphorus compounds will appear in a forthcoming publication.
- (8) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).
- (9) M. G. Newton, personal communication.
- (10) R. Hoffman, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972).
- (11) J. Devillers, D. Houalla, J. Roussel, and R. Wolf, *Org. Magn. Reson.*, in press.

Contribution from the Istituto di Chimica Generale e Inorganica, Università, Laboratorio CNR, Florence, Italy

Existence of Two Isomeric Forms of Chromium(II) Complexes with Saturated Macrocyclic Ligands

Andrea Dei* and Fabrizio Mani

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During the last 15 years a large number of 3d metal complexes with macrocyclic ligands have been synthesized and studied, in order to better understand their peculiar chemical properties, which often have biochemical interest.¹ The remarkable capacity of macrocyclic tetraamine ligands for stabilizing 3d metal ions in their low oxidation states² prompted us to investigate the coordinating behavior of such ligands toward chromium(II) halides, whose coordination compounds so far reported are not very numerous, owing to their instability toward oxidation.

This note reports the synthesis and characterization of chromium(II) complexes with two tetradentate macrocyclic ligands, *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (hence indicated as Me₂[14]aneN₄, I) and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Me₆[14]aneN₄, II).

Some chromium(II) complexes with the latter ligand have been already reported,³ but, to our knowledge, no detailed study on these complexes has been so far reported in literature.

Experimental Section

All reactions and operations were carried out under moisture-free nitrogen. Anhydrous chromium(II) halides, Me₂[14]aneN₄ and Me₆[14]aneN₄ were prepared as already described.⁴⁻⁶

The complexes were prepared by adding a concentrated dimethylformamide solution of the appropriate chromium(II) halide to the stoichiometric amount of the ligand dissolved in the minimum amount of the solvent. Upon mixing of the reactants, the solutions are intensely blue, but gradually they become purple with subsequent

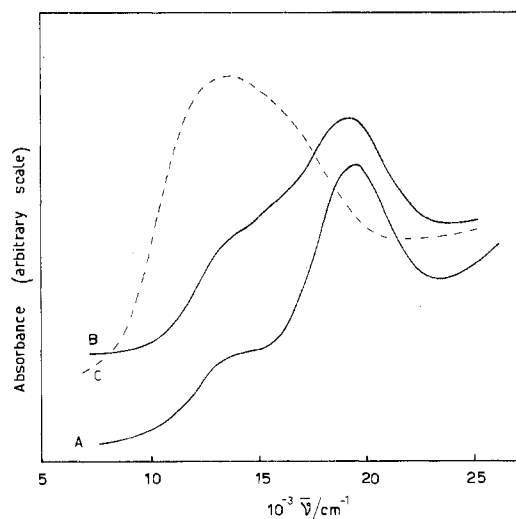
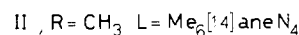
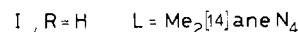
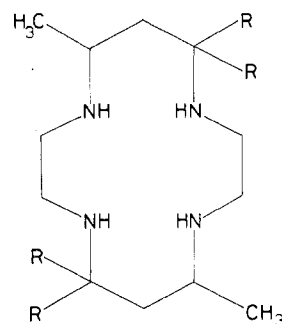


Figure 1. Diffuse reflectance spectra: A, Cr(Me₂[14]aneN₄)Cl₂; B, Cr(Me₆[14]aneN₄)Cl₂ (purple form); C, Cr(Me₆[14]aneN₄)Cl₂ (blue form).



precipitation of crystalline products of the same colour. The rate of turning from blue to purple is temperature dependent and markedly diminishes as the temperature is lowered. With the ligand Me₆[14]aneN₄, by keeping the blue solutions at 0–5 °C with an external ice bath, crystalline blue products having the same analytical formula as the corresponding purple compounds have been obtained.

Magnetic and spectrophotometric measurements were carried out using the apparatus already described⁷ on samples contained in suitable airtight containers (Gouy tube, uv and ir cells) filled in a drybox under inert atmosphere.

Results and Discussion

Purple complexes having the general formula CrLX₂ (L = Me₂[14]aneN₄, X = Cl, Br; L = Me₆[14]aneN₄, X = Cl, Br, I) have been obtained. With the latter ligand blue complexes with the same analytical formula as the corresponding purple compounds have been also obtained. All of the complexes reported here, which are listed in Table I together with their elemental analyses, are sensitive to aerial oxidation and atmospheric moisture. The complexes are sparingly soluble in the common organic solvents with the exception of dichloromethane and 1,2-dichloroethane; however, in spite of the care employed to prevent oxidation, these solutions decompose in a short time so that physical measurements are practically precluded.

Magnetic and electronic spectral data are reported in Table I. All of the complexes are high spin with effective magnetic moments at room temperature in the range usually found for four unpaired electrons.