Carbon 13 Nuclear Magnetic Resonance Spectroscopy of Cobalt(III) Complexes with Flexible Tetraamine Ligands

GEORGE R. BRUBAKER** and DAVID W. JOHNSON

Department of Chemistry, Illinois Institute of Technology, Chicago, Ill. 60616, U.S.A.

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The details of a systematic carbon 13 nuclear magnetic resonance study of cobalt(III) complexes with the tetraamine ligands 1,8-diamino-3,6-diaza-octane (2,2,2-tet), 1,9-diamino-3,6-diazanonane (2,2,3-tet), 1,9-diamino-3,7-diazanonane (2,3,2-tet) and 1,10-diamino-4,7-diazadecane (3,2,3-tet) are presented.

Carbon 13 NMR was found to be an extremely sensitive probe of the stereochemistry of this series of diamagnetic 'Werner' complexes. Our interpretation is based upon two parameters, the donation of electron density to the metal and the steric perturbation required for coordination.

The stereochemistry of uns-cis(Co(2,2,3-tet)Val)$^{++}$ *is assigned based upon the carbon 13 NMR spectrum of the complex.*

Introduction

Cobalt(III) complexes with tetradentate ligands are known in each of three possible topologies (Fig. 1) [1]. Of these structural isomers, the *trans* and
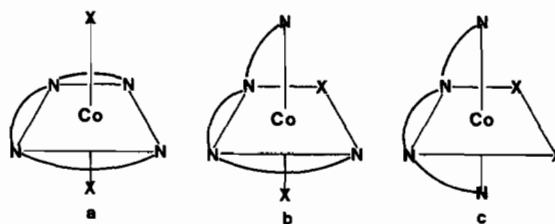

Fig. 1. The topology of six coordinate complexes with flexible tetradentate ligands. a) *trans*, b) *uns-cis*, c) *s-cis*.

uns-cis forms are the most common, in part due to lower strain energies [2], however the *s-cis* form is also well known [1]. The different symmetry of the complexes often permits determination of stereochemistry from the electronic spectrum. In addition, other methods including vibrational spectroscopy and proton NMR, have been used with some success to determine stereochemistry. These methods suffer, however, from a lack of sensitivity, especially in complexes with unsymmetrical ligands [3].

In the course of our continuing study of the stereochemistry of six coordinate transition metal complexes, we have investigated a large variety of cobalt(III) complexes with various tetraamine ligands (some common tetraamine ligands are shown in Table I). We have also recently reported a proton NMR and strain energy minimization study of some cobalt(III) complexes with the unsymmetrical tetraamine 1,9-

TABLE I. Some Flexible Tetraamine Ligands.

Name	Structure	Abbreviation
1,8-diamino-3,6-diazaoctane	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	2,2,2-tet (Trien)
1,9-diamino-3,7-diazanonane	$NH_2CH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2NH_2$	2,3,2-tet
1,9-diamino-3,6-diazanonane	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2NH_2$	2,2,3-tet
1,9-diamino-3,6-diaza-8-methylnonane	$NH_2CH_2CH_2NHCH_2CH_2NHCH(CH_3)CH_2NH_2$	8-methyl 2,2,3-tet
1,10-diamino-4,7-diazadecane	$NH_2CH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2NH_2$	3,2,3-tet

diamino-3,6-diazanonane (2,2,3-tet) [4]. This study was undertaken partially to unravel the stereochemistry of complexes with 2,2,3-tet, but also revealed some interesting generalizations.

Carbon 13 NMR has become an important tool for the organic chemist for structure elucidation [5]. This tool, however, has only recently found common use among inorganic chemists [6]. The carbon-13 NMR spectra of some cobalt(III) complexes with an assortment of diamine-N,N′-diacetate [7] and diamine-N,N,N′-triacetate ligands [8], have indicated the usefulness of carbon 13 NMR in the determination of inorganic stereochemistry.

In this report, we describe a detailed carbon-13 NMR study of cobalt(III) tetraamine complexes and an interpretation based upon two parameters, the decreased shielding of the carbon atoms due to the metal ion, and the increased shielding due to the steric demands of coordination to the metal.

Experimental

Syntheses

1,9-diamino-3,6-diaza-8-methylnonane (8-methyl-2,2,3-tet): 8-methyl-2,2,3-tet was prepared by the method of Brubaker, Jarke and Brubaker [4] substituting methacrylonitrile for acrylonitrile.

Trans-Dichloro(1,9-diamino-3,6-diaza-8-methyl-nonane)cobalt(III) chloride (*trans*-(Co(8-methyl-2,2,3-tet)Cl$_2$)Cl) was prepared by the method of Brubaker, Jarke and Brubaker substituting 8-methyl-2,2,3-tet for 2,2,3-tet. All other complexes were prepared by previously published methods [9].

NMR Spectra

Carbon 13 NMR spectra were measured with a Varian CFT-20 NMR spectrometer in the deuterium locked, proton noise decoupled mode. Samples were dissolved in a minimum of DMSO d$_6$ (99.5 atom percent D, Aldrich Chemical), placed in 10 mm NMR tubes (Wilmad) and spun in a jet of air. A spectral width of 4000 Hz (except in the case of amino acid complexes where 5000 Hz was used) covered by 8192 data points was used. Transients were collected until an acceptable signal to noise ratio was achieved (400 to 70,000 transients). All chemical shifts are reported relative to tetramethylsilane.

Results and Discussion

The carbon 13 NMR spectrum of these ligands and complexes are characterized by excellent signal to noise ratios and narrow lines (5 Hz). The spectra do not suffer significantly from coupling with either nitrogen or cobalt, which often makes the proton

NMR spectra of cobalt(III) amine complexes difficult to interpret [3, 10].

The carbon 13 NMR spectra normally exhibit a heptet centered at 39.6 ppm, arising from the solvent. The narrow line widths associated with the spectra minimizes the problem of solvent masking. All of the resonance signals can be identified, though occasionally one line appears at the same chemical shift as one of the solvent peaks, and must be found by comparing solvent peak intensities. The number of resonances is always consistent with the number of carbon atoms and the symmetry of the complex.

The 1,8-Diamino-3,6-diazaoctane System

Complexes of 2,2,2-tet (triethylenetetramine) are known to exist in all three possible stereochemistries (Fig. 1). The carbon 13 NMR spectra of a series of *uns-cis* complexes have been studied [11], showing the expected six resonance signals from the tetra-amine. Complexes with *trans* and *s-cis* stereochemistries have also been studied [12] displaying the expected three resonances, consistent with the twofold symmetry of the complexes. The *trans* and *s-cis* complexes can, however be distinguished by chemical shift differences, even though the number of resonances are the same. These differences can be attributed to the different environments of the carbon atoms in the complexes.

The 1,9-Diamino-3,7-diazanonane (2,3,2-tet) System

The ^{13}C NMR spectrum of 2,3,2-tet in DMSO was assigned using the ^{13}C NMR spectra of several simple aliphatic diamines as models [13]. These spectra indicate that the carbon atom with the greatest shielding, is the unique carbon atom which is β* to the amine nitrogen (all other carbons are directly bonded to nitrogen). The signal at the smallest shielding is assigned to the carbon atoms α to a secondary amine and only one carbon atom away from another nitrogen. The other carbon atoms α to secondary amines appear somewhat more shielded and the carbon atoms α to primary amines appear at the greatest shielding among the carbons α to nitrogen (see Fig. 2).

The chemical shift data for some cobalt(III) complexes with 2,3,2-tet are shown in Table II along with the chemical shift difference (denoted as Δ in Table II) between a given peak in the complex and the same peak in the free ligand. The ^{13}C NMR spectrum of *trans*-(Co(2,3,2-tet)Cl$_2$)Cl exhibits four resonances with approximate relative intensities of

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*For the sake of simplicity, carbon atoms have been labeled by their position relative to the amine nitrogens. Carbon atoms directly bonded to the nitrogen atoms are labeled α and those carbon atoms one carbon atom away from the nearest nitrogen atom are labeled β.

TABLE II. ^{13}C NMR Data for (2,3,2-tet) Complexes.

Compound	C_1, C_7	Δ	C_2, C_6	Δ	C_3, C_5	Δ	C_4	Δ
(2,3,2-tet)	41.56	–	52.83	–	47.78	–	30.27	–
trans (Co(2,3,2-tet)Cl$_2$)$^+$	42.41	0.85	54.67	1.84	47.87	0.09	28.04	−2.23
Uns-cis (Co(2,3,2-tet)CO$_3$)$^+$	42.42	0.86	54.66	1.83	48.97	1.19	22.89	−7.38
	42.20	0.64	49.70	−3.13	46.71	−1.07		
uns-cis (Co(2,3,2-tet)ala)$^{++}$	42.91	1.35	54.64	1.81	47.96	0.18	22.16	−8.11
*	42.64	1.08	48.81	−4.02	44.14	−3.64		

*Carbon from alanine at 53.04 ppm.

$$NH_2 \overset{1}{CH_2} \overset{2}{CH_2} NHCH_2 \overset{3}{CH_2} \overset{4}{CH_2} \overset{5}{CH_2} NHCH_2 \overset{6}{CH_2} \overset{7}{CH_2} NH_2$$
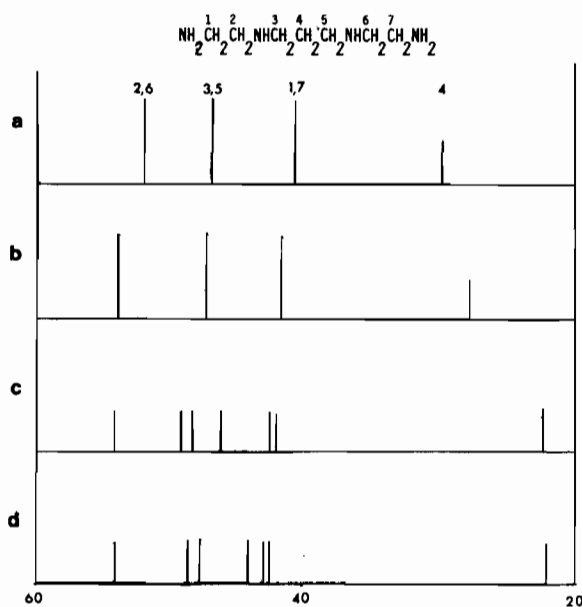
Fig. 2. ^{13}C NMR spectra for the 2,3,2-tet system. a) 2,3,2-tet, b) *trans*(Co(2,3,2-tet)Cl$_2$)Cl, c) *uns-cis*(Co(2,3,2-tet)CO$_3$)I, d) *uns-cis*(Co(2,3,2-tet)ala)I$_2$.

2:2:2:1**. The number of signals is precisely as is predicted from symmetry considerations. The relative positions of the resonances are shown in Fig. 2.

**While the intensities in a Fourier transform NMR experiment depend upon relaxation times and the nuclear Overhauser effect (NOE), in addition to number of atoms, the carbon atoms in the compounds of this study are sufficiently similar that approximate comparisons of intensity can be made.

TABLE III. Selected X-ray Data for 2,3,2-tet Complexes.

Atom (distance or angle)		X-ray data Cu(2,3,2-tet)	Chemical shift (ppm from TMS)
C_1	N_1-C_1	1.478	
	C_1-C_2	1.51	42.41
	⟨$N_1C_1C_2$	106.6	
C_2	C_1-C_2	1.51	
	C_2-N2	1.486	54.67
	⟨$C_1C_2N_2$	108.7	
C_3	N_2-C_3	1.520	
	C_3-C_4	1.50	47.87
	⟨$N_2C_2C_4$	111.4	
C_4	C_3-C_4	1.50	
	C_4-C_5	1.52	28.04
	⟨$C_3C_4C_5$	115.0	
C_5	C_4-C_5	1.52	
	C_5-N_3	1.489	47.87
	⟨$C_4C_5N_3$	111.7	
C_6	N_3-C_6	1.479	
	C_6-C_7	1.53	54.67
	⟨$N_3C_6C_7$	107.7	
C_7	C_6-C_7	1.53	
	C_7-N_4	1.476	42.41
	⟨$C_6C_7N_4$	107.9	

The carbon atom signals of the five membered chelate rings appear at significantly higher chemical shift (smaller shielding) than the carbons in the free ligand. This decrease in shielding is due to the donation of electron density to the metal ion (similar to the shielding observed for the methylenes in ethylenediamine-N,N'-diacetate complexes [7]). Examination of some crystallographic for Cu(2,3,2-

TABLE IV. Selected Crystallographic and ^{13}C NMR Data for 3,2,3-tet Complexes.

Atom		Crystal Structure		NMR Spectrum	
		trans Complex	*uns-cis* Complex	*trans* Complex	*uns-cis* Complex
C_1	N_1-C_1	1.489	1.478		
	C_1-C_2	1.510	1.501	38.58	37.40
	$\langle N_1C_1C_2$	111.5	112		
C_2	C_1-C_2	1.510	1.501		
	C_2-C_3	1.515	1.505	26.77	26.69
	$\langle C_1C_2C_3$	113.7	112.7		
C_3	C_2-C_3	1.515	1.505		
	C_3-N_2	1.483	1.472	48.21	46.78
	$\langle C_2C_3N_2$	112.0	112.9		
C_4	N_2-C_4	1.482	1.493		
	C_4-C_5	1.512	1.493	52.55	52.23
	$\langle N_2C_4C_5$	107.1	107.0		
C_5	C_4-C_5	1.512	1.493		
	C_5-N_3	1.495	1.479	52.55	47.02
	$\langle C_4C_5N_3$	107.3	N.A.		
C_6	N_3-C_6	1.479	1.507		
	C_6-C_7	1.508	1.510	48.21	43.95
	$\langle N_3C_6C_7$	112.7	113.4		
C_7	C_6-C_7	1.508	1.510		
	C_7-C_8	1.510	1.484	26.77	21.07
	$\langle C_6C_7C_8$	113.5	113.5		
C_8	C_7-C_8	1.510	1.484		
	C_8-N_4	1.481	1.500	38.56	35.81
	$\langle C_7C_8N_4$	112.1	112.4		

tet)(ClO$_4$)$_2$ [14] shows the nearly 'ideal' geometries of the carbons in the five membered chelate rings (*i.e.*, tetrahedral bond angles and C–C bond lengths of 0.154 nm and C–N bond lengths of 0.147 nm).

The carbon-13 NMR signals from the α carbon atoms of the six membered chelate ring appear at nearly the same chemical shift as in the free ligand (a difference of 0.09 ppm). The β carbon of the six membered chelate ring appears with an increase in shielding. Examination of the X-ray data (Table III) indicates a degree of steric compression of the carbon atoms in the six membered chelate ring. The somewhat compressed bond distances and larger than normal bond angles would be expected to increase the shielding at these carbon atoms [15]. The α carbon atoms of the six membered chelate ring appear to be influenced by both the shift of electron density to the metal ion (decreasing shielding) and the steric compression (increasing shielding) leading to only a small change in chemical shift. The β carbon atom of the six membered ring is influenced primarily by the steric compression

(increasing shielding). The donation of electron density toward the metal ion is expected to be smaller at this carbon due to the greater distance (both through space and number of chemical bonds) between it and the metal ion.

It is evident from the ^{13}C NMR spectra of the *uns-cis* complexes (Fig. 2, Table II) that the symmetry of the complex has decreased, the expected consequence of the *uns-cis* stereochemistry. Each of the resonance signals which represented two carbon atoms in the *trans* complex is split into two distinct signals with a shift inequivalence which varies from 0.2 to 6 ppm*.

Examination of the spectra (Fig. 2, Table II) reveals a major change in only some carbon atoms. The carbons α to primary amines show only a small chemical shift inequivalence (0.24–0.27 ppm),

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*The chemical shift inequivalence is the difference in chemical shift between two resonances which were equivalent in the free ligand and *trans* complex.

TABLE V. ^{13}C NMR Data for Complexes of (3,2,3-tet)$_x$.

Complex	C_1, C_8	Δ	C_2, C_7	Δ	C_3, C_6	Δ	C_4, C_5	Δ
3,2,3-tet	40.02	–	33.80	–	47.31	–	49.30	–
trans (Co(3,2,3-tet)Cl$_2$)$^+$	38.56	−1.46	26.77	−7.03	48.21	0.90	52.55	3.25
trans (Co(3,2,3-tet)Br$_2$)$^+$	39.30	−0.72	26.70	−7.60	49.08	1.77	52.86	3.56
uns-cis (Co(3,2,3-tet)CO$_3$)$^+$	38.87	−1.15	26.24	−7.56	47.27	−0.04	52.23	2.93
	38.23	−1.79	21.93	−11.87	45.54	−1.77	48.65	−0.65
uns-cis (Co(3,2,3-tet)Acac)$^{++}$	37.40	−2.62	26.69	−7.11	46.78	−0.53	52.53	2.93
	35.31	−4.71	21.07	−12.73	43.95	−3.36	47.02	−2.28

suggesting only a small change in environment. The other carbon atoms in the five membered chelate ring show large shift inequivalences. One of these carbon atoms remains at approximately the same chemical shift, while the other carbon atom appears with increased shielding, indicating a significant steric compression.

The α carbon atoms of the six membered chelate ring also show a considerable chemical shift inequivalence (2.82–3.83 ppm). One of these two carbon atoms appears at about the same chemical shift as in the *trans* complex with the other appearing with a higher shielding. The β carbon of the six membered chelate ring also appears with an increased shielding. These chemical shift changes indicate a major change in stereochemistry of the six membered chelate ring. A change in stereochemistry has also been observed in circular dichroism studies [16]. We attribute this change to the adoption of a skew boat conformation of the six membered chelate ring.

The 1,10-Diamino-4,7-diazadecane (3,2,3-tet) System

The carbon-13 NMR spectrum of the free ligand (Table IV) was assigned by a method similar to 2,3,2-tet. The β carbon atom signals appear at 33.80 ppm, the carbons α to primary amines appear at 40.02 ppm, the carbons α to the secondary amines and two carbon atoms adjacent to the primary amines (C_3 and C_6) appear at 47.31 and the remaining carbon atoms (C_4, C_5) appear at 49.30 ppm.

The ^{13}C NMR of *trans*(Co(3,2,3-tet)Cl$_2$)Cl shows both the decreased shielding from the donation of electron density toward the metal ion, and the increased shielding due to steric perturbations. Crystallographic data (shown in Table IV) [17] for this complex shows this steric perturbation, espe-
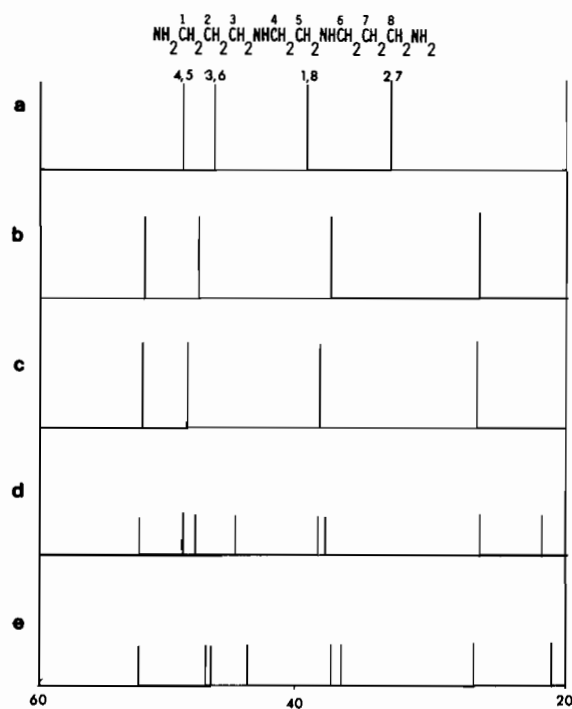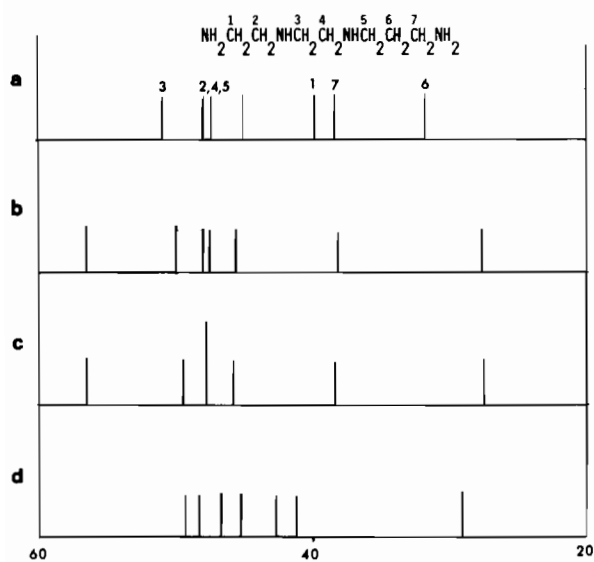

Fig. 3. ^{13}C NMR Spectra for the 3,2,3-tet system. a) 3,2,3-tet, b) *trans*(Co(3,2,3-tet)Cl$_2$)Cl, c) *trans*(Co(3,2,3-tet)Br$_2$)-ClO$_4$, d) *uns-cis*(Co(3,2,3-tet)CO$_3$)I, e) *uns-cis*(Co(3,2,3-tet)acac)I$_2$.

cially in the six membered chelate rings. The steric perturbation appears in the β carbons and the carbons α to primary amines as increases in shielding. The resonance signals from the carbon atoms α to secondary amines and in the six membered chelate rings appear at greater chemical shifts than in the free ligand, but the difference is smaller than that observ-

TABLE VI. ^{13}C NMR Data for 2,2,3-tet Complexes.

Complex	C_1	C_2	C_3	C_4	C_5	C_6	C_7
(2,2,3-tet)	40.06	47.86	51.10	47.53	45.78	32.10	38.67
trans (Co(2,2,3-tet)Cl$_2$)$^+$	46.31	48.20	56.77	50.07	48.53	27.56	38.08
trans Co(2,2,3-tet)(OAc)$_2^{2+}$	45.81	47.20	56.49	48.78	47.20	27.02	37.96
uns-cis (Co(2,2,3-tet)Val)$^{++}$	42.74	46.10	48.90	47.74	45.22	29.85	41.26

Fig. 4. ^{13}C NMR spectra for the 2,2,3-tet system. a) 2,2,3-tet, b) trans(Co(2,2,3-tet)Cl$_2$)Cl, c) trans(Co(2,2,3-tet)(OOCCH$_3$)$_2$)ClO$_4$, d) uns-cis(Co(2,2,3-tet)Val)I$_2$.

Fig. 5. ^{13}C NMR spectra of a) trans(Co(2,2,3-tet)Cl$_2$)Cl and b) trans(Co(8-methyl-2,2,3-tet)Cl$_2$)Cl (the signal from the methyl group appears at 16.77 ppm from TMS).

ed for the carbon atoms of the five membered chelate ring.

Crystallographic studies [18] and strain energy minimization calculations [2] indicate a greater bond length and angle distortion for the *uns-cis* than the *trans* stereochemistry. The proton NMR spectra [3] of these complexes indicate a substantial difference in the environment of the amine protons, and the ^{13}C NMR spectra show the expected inequivalence of the carbon atoms. The relative changes in the spectra are shown in Fig. 3.

The NMR signals of the carbon atoms of the five-membered chelate ring reflect significant changes in the environment of one of these atoms (see Fig. 3). The shift inequivalence of these carbons is 4.16 to 5.21 ppm. The carbon atoms α to the primary amines show a shift inequivalence of 0.64 to 2.09 ppm. The
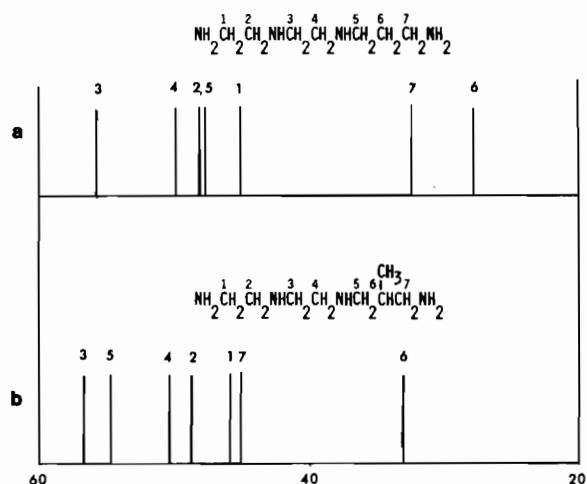
resonance signals of the other carbon atoms of the six membered chelate ring show larger shift inequivalences (5.31 to 5.62 ppm for the β carbons and 1.77 to 2.83 ppm for the carbon atoms α to secondary amines) reflecting the additional steric perturbation of the change in stereochemistry. Structural data (Table IV) show these steric perturbations at 'abnormal' bond distances and bond angles especially around C_7 (one of the β carbons) and C_5 (one carbon in the five membered chelate ring). The atoms showing the largest shift inequivalence in the ^{13}C NMR also have the largest change in bond distances and angle in the X-ray crystal structure (Table IV).

The 1,9-Diamino-3,6-diazanonane (2,2,3-tet) System

The introduction of an unsymmetrical ligand introduces another degree of complexity in the assignment of stereochemistry regardless of the method used. First, the number of possible isomers

is increased, and second, the differences between some groups of isomers are small. Thus, a detailed assignment of stereochemistry is difficult regardless of the method used.

The free ligand spectrum of 2,2,3-tet (Table VI, Fig. 4) is sufficiently complicated, due to the decreased symmetry, that an assignment is difficult and ambiguous. The resonance signal with the smallest chemical shift can be ascribed to the β carbon, the next two signals (increasing in chemical shift), are the carbons α to primary amines with the carbons α to secondary amines appearing at the highest chemical shift. The differences in ^{13}C chemical shift between atoms α to secondary amines is not sufficient to permit individual assignment.

The ^{13}C NMR of the complex, *trans*(Co(2,2,3-tet)Cl$_2$)Cl, is sufficiently complicated that an adequate assignment is not possible. To reduce this ambiguity, the ^{13}C NMR spectrum of *trans*(Co(8-methyl-2,2,3-tet)Cl$_2$)Cl was also examined. A comparison of the two spectra is shown in Fig. 5. It can be seen from the spectra of the two *trans* complexes, that the chemical shifts of four of the resonance signals change only slightly with the addition of the methyl group. These signals must arise from the carbons of the five membered chelate rings. The signals from the six membered chelate ring can be assigned to the remainder of the spectrum. The carbon with the highest chemical shift is assigned to C3 of 2,2,3-tet and the signal at 38.08 ppm in *trans*(Co(2,2,3-tet)Cl$_2$)Cl is assigned to the carbon α to the primary amine of the six membered chelate ring. The signal at 46.31 can then be assigned to the other carbon α to a primary amine (in the five membered chelate ring). A tentative assignment of the remainder of the spectrum is shown in Fig. 4.

Complexes of 2,2,3-tet with the *uns-cis* stereochemistry have also been synthesized. These complexes may exist in either of two structures (Fig. 6) which are indistinguishable in electronic or circular dichroism spectra [3]. Previously published proton NMR spectra and strain energy minimization calculations [4] indicate that isomer a, Fig. 6, has the lower strain energy. We have endeavored to apply ^{13}C NMR spectroscopy to distinguish between these possibilities.

Our stereochemical assignment is based upon the signals which change most with the change in stereochemistry. The largest change in chemical shift is observed for the carbon atom with the highest chemical shift (C$_3$). This atom would be expected to have the largest change in steric environment if the adopted *uns-cis* isomer has the five membered chelate ring perpendicular to the plane of the three amine nitrogen atoms.

Other carbon atoms with major changes in environment are those α to the primary amines and the β carbon atom. The carbon α to the primary
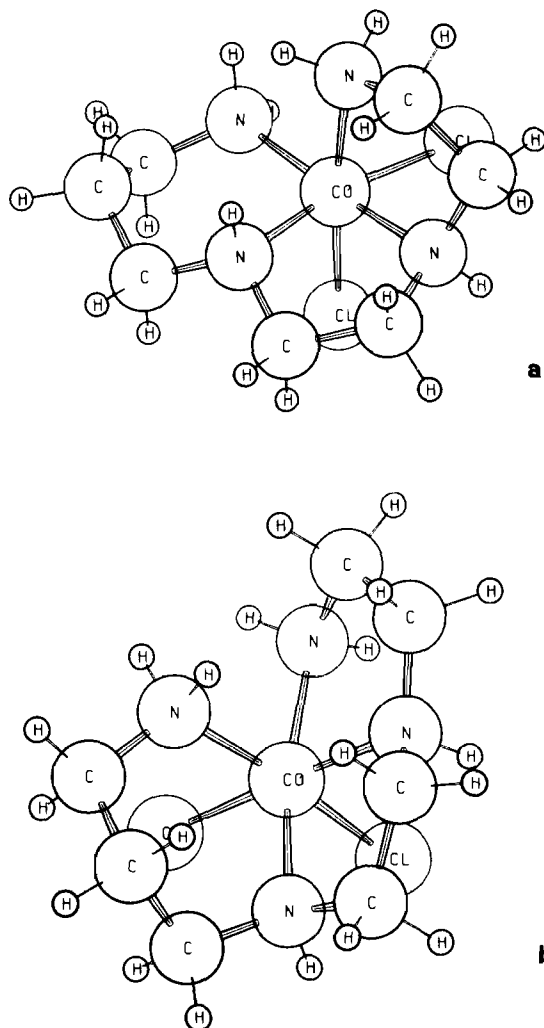
Fig. 6. Two *uns-cis* isomers of (Co(2,2,3-tet)X$_2$)$^+$. a) The 2,2,3 isomer, with the six-membered ring coplanar with the secondary amine nitrogens and cobalt atoms. b) the 2,2,3 isomer, with the five-membered ring coplanar with the secondary amine nitrogens and cobalt atoms.

amine of the five membered chelate ring (C$_1$) shows an increase in shielding by 3.07 ppm, indicating a significant steric compression. The carbon atom α to the primary amine in the six membered chelate ring appears at a higher chemical shift (3.18 ppm) than in the *trans* complex. The β carbon also appears at a higher chemical shift (2.29 ppm) than in the *trans* complex, indicating a release in ring strain in the six membered chelate ring. The increased strain at C$_1$ and C$_3$ along with the release in strain in the six membered chelate ring indicate that the adopted stereochemistry has the five membered chelate ring perpendicular to the plane of the cobalt and three amine nitrogens.

The ^{13}C NMR spectrum of the *uns-cis* complex indicates that the six membered chelate ring can

adopt a more ideal geometry because of the reduced steric demands of the *uns-cis* stereochemistry. The spectra are also consistent with the lower strain energy of the *uns-cis* complex when compared with the *trans* isomer, in agreement with energy minimization calculations [4].

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