HOMO–LUMO arguments have been used to describe the Ag^+–benzene and Ag^+–ethylene interactions [R. S. Mulliken and W. B. Person, "Molecular Complexes", Wiley-Interscience, New York, N.Y., 1969, Chapter 17].
(30) (a) A. R. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.*, **4**, 788 (1965); (b) D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *J. Am. Chem. Soc.*, **95**, 3875 (1973).
(31) J. S. Miller, D. G. Marsh, and J. W. Lewicki, unpublished results.
(32) The larger spacings of O_5–O_3' and O_1–O_6' can be rationalized by the weighted contribution of both back-bonding overlaps depicted in Figures 2 and 3.
(33) R. Mattes and K. Krogmann, *Z. Anorg. Allg. Chem.*, **332**, 247 (1964).
(34) Unfortunately the standard deviations for the bond lengths and angles are not reported.
(35) E. G. Cox, W. Wardlow, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).
(36) J. H. Perlstein, private communication.
(37) K. W. Browall, T. Bursh, L. V. Interrante, and J. S. Kasper, *Inorg. Chem.*, **11**, 1800 (1972); K. W. Browall, L. V. Interrante, and J. S. Kasper, *J. Am. Chem. Soc.*, **93**, 6289 (1971).
(38) Although close approach of sulfur atoms (~3.0 Å) has been characterized,[37] smaller interplanar separations (<2.9 Å) appear to be necessary for allowing strong overlap and band formation.[1]
(39) D. Coucouvanis, private communication.
(40) HOMO–LUMO intermolecular back-bonding considerations have also revealed 12 back-bonding overlaps for $M(HDMG)_2$ (M = Ni, Pd, Pt; H_2DMG = dimethylglyoxime) when adjacent planes are rotated by 90° and a maximum number of four back-bonding overlaps when adjacent molecular planes are rotated by 180° for $M(CO)_2(acac)$ (M = Rh, Ir; Hacac = acetylacetone). These and other results will be discussed in subsequent papers.

Contribution from the Department of Chemistry,
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Structural Changes in Cobalt(II) Complexes Resulting from Nonsteric Substituent Effects with Potentially Five-Coordinate Ligands[1]

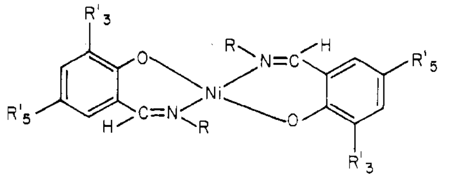
R. H. NISWANDER and L. T. TAYLOR*

Received November 20, 1975 AIC508421

Linear, potentially pentadentate Schiff base ligands derived from various salicylaldehydes (*R*-SAL) and bis(3-aminopropyl) ether (DAPE), bis(3-aminopropyl) sulfide (DAPS), or bis(3-aminopropyl)phenylamine (PhDPT) represent a series of chelate compounds in which the central donor atom is varied. Cobalt(II) complexes of these ligands have been isolated and characterized via elemental analysis, infrared–visible spectra, and magnetic susceptibility. The structure of these complexes depends upon the aromatic substituents in the molecule. This is the first report of structural changes in complexes of this type resulting from nonsteric substituent effects. The results are discussed in terms of the electronic effect of the substituents.

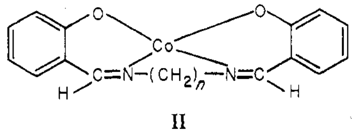
Introduction

The stereochemical and structural features imposed on a metal complex by Schiff base ligands have been the subject of numerous studies.[2a] Most of the systematic studies that have been carried out have investigated the steric effects of ligand substituents. Many of these studies have dealt with the coordination of nickel(II) and cobalt(II) ions. A good example of these investigations is illustrated by the nickel(II) salicylaldimine complexes shown in structure I. Upon increasing the bulkiness of the R group, the complex stereochemistry in the solid state changes from a diamagnetic square-planar structure to a paramagnetic tetrahedral arrangement. In general the effect of a benzene ring substituent, R′, on the stereochemistry of these complexes is minimal[2b] (R′ = H, 3-CH_3, 5-CH_3, 3-Cl, 3-Br, 3-NO_2, 3,5-benzo, 5-NO_2, 3,4-benzo).

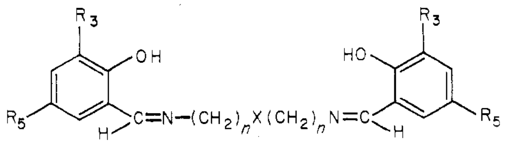


I

A ligand-promoted configurational change has also been observed with linear tetradentate ligands derived from salicylaldehyde and long-chain diamines bound to cobalt(II)[3] (structure II). With increasing chain length joining azomethine linkages, tetrahedral geometries become favored over square-planar ones. The effect of ring substitution on the resulting complex stereochemistry was not investigated, though it might be concluded that the stereochemical effect of electron-withdrawing and electron-donating groups on these salicyladehyde-related ligands is negligible. This conclusion is supported by the fact that Zn(II), Cu(II), Ni(II), Co(II), and Mn(II) complexes incorporating linear pentadentate ligands derived from variously substituted salicylaldehydes and either bis(3-aminopropyl)amine, $H_2RSALDPT$ (IIIa), or bis(3-aminopropyl)methylamine, $H_2RSALMeDPT$ (IIIb), have been shown to be isomorphous[4] (R = H, 5-CH_3, 5-C_2H_5, 3,4-benzo, 5,6-benzo, 5-Cl, 3-Cl, 3,5-Cl_2, 5-Br). Also, $H_2RSALDAES$ (IIId), a potentially pentadentate ligand, was shown to produce four-coordinate complexes with cobalt(II) regardless of the substituent[5] (R = H, 5-NO_2, 5-Br, 5-CH_3, 3-$(CH_3)_2CH$). Studying a related group of potentially pentadentate ligands we have noticed differences in the solid-state structure of cobalt(II) complexes which appear to depend on the coordinating properties of the central donor.[6] If the central donor is P-CH_3 (IIIc, R = H) or N-C_6H_5 (IVc, R and R′ = H), five-coordinate cobalt complexes are observed, while ether (IVb, R = H) and thioether (IVa, R = H) donors result in cobalt(II) complexes which are four-coordinate



II



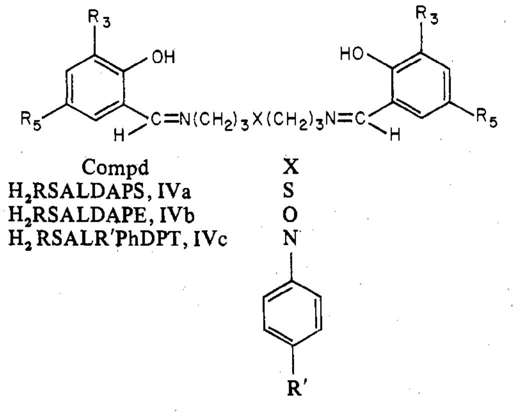
IIIa, $H_2RSALDPT$, X = NH, *n* = 3
b, $H_2RSALMeDPT$, X = NCH_3, *n* = 3
c, $H_2RSALDAPP$, X = PCH_3, *n* = 3
d, $H_2RSALDAES$, X = S, *n* = 2

Table I. Magnetic and Analytical Data for the Cobalt(II) Complexes

Complex	Color	μ_{eff},[a] μ_B	% C		% H		% N	
			Calcd	Found	Calcd	Found	Calcd	Found
Co(3-CH$_3$OSALDAPE)	Yellow	4.32	57.77	57.37	5.69	5.84	6.13	5.98
Co(5-CH$_3$OSALDAPE)	Orange	4.23	57.77	58.15	5.69	5.90	6.13	6.30
Co(5-ClSALDAPE)	Tan	4.38	51.50	51.60	4.29	4.18	6.00	6.30
Co(5-BrSALDAPE)	Brown	4.39	43.24	43.02	3.60	3.58	5.05	5.09
Co(3-NO$_2$SALDAPE)	Orange-yellow	4.38	49.28	49.02	4.11	4.01	11.50	11.53
Co(3-CH(CH$_3$)$_2$SALDAPS)	Brown	4.49	64.86	64.79	7.12	7.40	5.82	6.10
Co(5-ClSALDAPS)	Tan	4.33	49.79	49.76	4.15	4.26	5.81	5.75
Co(5-BrSALDAPS)	Brown	4.32	42.03	41.76	3.50	3.11	4.90	4.94
Co(3-CH$_3$OSALPhDPT)	Yellow	4.21	63.18	62.95	5.87	5.60	7.89	8.14
Co(5-CH$_3$OSALPhDPT)	Orange	4.32	63.18	62.81	5.87	6.15	7.89	7.91
Co(5-ClSALPhDPT)	Green-tan	4.28	57.67	57.79	4.62	4.49	7.76	7.74
Co(SAL-*p*-ClPhDPT)	Yellow-brown	4.22	61.60	61.20	5.13	4.91	8.29	8.41
Co(SAL-*p*-CH$_3$OPhDPT)	Tan	4.34	64.54	64.47	5.78	5.86	8.37	8.25
Co(SAL-*p*-CH$_3$PhDPT)	Yellow	4.40	65.82	66.13	6.12	5.99	8.86	8.75
Co(3-NO$_2$SAL-*p*-ClPhDPT)	Orange-tan	4.39	52.31	52.05	4.02	4.02	11.74	11.82

[a] Values of solid-state compounds at room temperature (22–25 °C).

tetrahedral. We wish now to report that, in those ligands containing a weak central donor, ring substituents profoundly determine whether the metal is four- or five-coordinate. The general features of these ligands are shown in structure IV.



Compd	X
H$_2$RSALDAPS, IVa	S
H$_2$RSALDAPE, IVb	O
H$_2$RSALR'PhDPT, IVc	N

R = 3-CH$_3$O, 5-CH$_3$O, 3-NO$_2$, 5-Cl, 5-Br, 3-CH(CH$_3$)$_2$
R' = *p*-Cl, *p*-CH$_3$O, *p*-CH$_3$

Experimental Section

Materials. The ligands were prepared in an alcoholic medium by condensing the substituted salicyladehyde with a diamine containing the ether (DAPE), thioether (DAPS), or phenylamine (PhDPT) donor. These were usually not isolated but deprotonated with alcoholic KOH and then complexed with an aqueous solution of cobalt(II) acetate tetrahydrate. 3-Isopropylsalicylaldehyde was prepared according to the procedure described by the Duff reaction.[7] The other substituted salicylaldehydes were obtained from Eastman Organic Chemicals Co. or Aldrich Chemical Co. DAPE was prepared by a catalytic hydrogenation similar to that reported by Modest et al.[8] The preparation of DAPS followed the Gabriel synthesis.[9] PhDPT and its derivatives were prepared by catalytically reducing the corresponding cyano compound.[10] All other chemicals were reagent grade or equivalent. All solvents used in the preparations were deaerated with N$_2$.

Preparation of the Complexes. A 250-ml round-bottom flask was fitted with a pressure-equalizing dropping funnel and nitrogen intake. A magnetic stirring bar was placed in the flask along with a solution of 0.02 mol of the appropriate salicyladehyde in 50 ml of 2-propanol. A solution of 0.01 mol of the diamine in 50 ml of 2-propanol was then added with stirring. A yellow color immediately resulted and the mixture was brought to reflux under nitrogen. The flask was then allowed to cool and 0.02 mol of KOH in 20 ml of deoxygenated methanol was added dropwise. After addition of the base, 0.01 mol of Co(OAc)$_2$·4H$_2$O in 15 ml of deoxygenated H$_2$O was added slowly. After addition of the metal acetate the precipitate was stirred 1–2 h. With the phenylamine complexes, tarring was sometimes observed, but it can be prevented by cooling the flask to 0 °C before adding the metal acetate. After stirring of the precipitate, the flask was stoppered and placed in an inert-atmosphere box. The flask was then opened and the contents filtered, washed with hexane, and dried in vacuo at room temperature for 12 h.

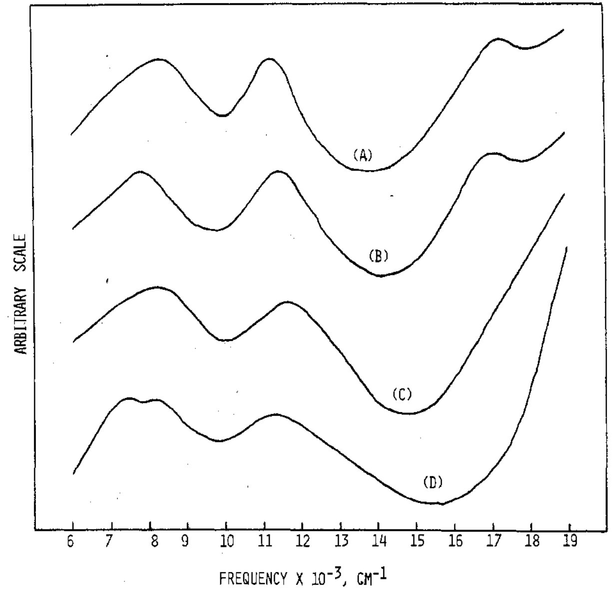


Figure 1. Solid-state electronic absorption spectra of Co(SALPhDPT) (A), Co(5-ClSALDAPE) (B), Co(5-BrSALDAPS) (C), and Co(3-NO$_2$SALDAPE) (D).

Physical Measurements. Elemental analyses were performed using a Perkin-Elmer Model 240 C, H, and N analyzer. Infrared spectra were obtained on a Beckman 20 AX recording spectrophotometer over the region 4000–300 cm^{-1}. Samples were prepared as Nujol mulls. Magnetic susceptibility data were obtained by the Faraday method at room temperature and at several different magnetic fields. Ultraviolet, visible, and near-infrared spectra were measured with a Cary 14 recording spectrophotometer. Molecular weight data were furnished by Galbraith Microanalytical Laboratories.

Results and Discussion

A series of cobalt(II) complexes has been prepared from linear potentially pentadentate ligands. Both the central donor and the substituents have been varied. The analytical data (Table I) support the proposed composition, CoL, were L is the deprotonated form of the ligand. All compounds are obtained unsolvated and do not react with oxygen in the solid state. The color and the solubility of the compounds depend both upon the central donor and upon the various substituents.

The room-temperature magnetic susceptibility data (Table I) suggest tetrahedral or high-spin five-coordinate geometry. In our previous report,[6] it was shown that the unsubstituted compounds also have magnetic moments in this range. The

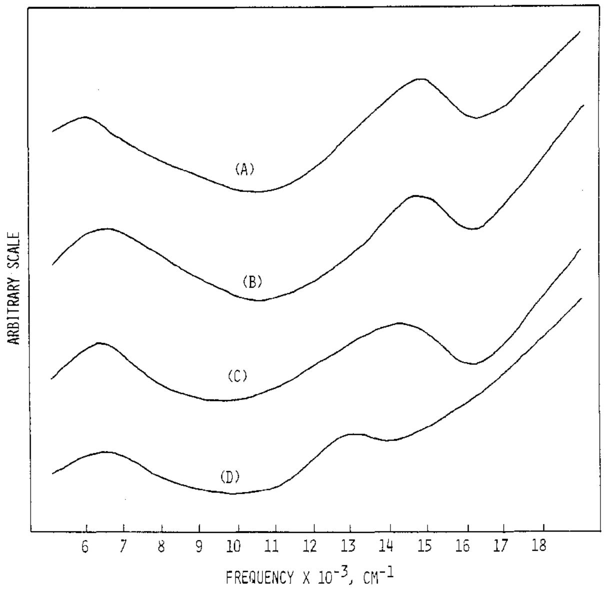


Figure 2. Solid-state electronic absorption spectra of Co(SALDAPS) (A), Co(SALDAPE) (B), Co(3-CH_3OSALPhDPT) (C), and Co(5-CH_3OSALPhDPT) (D).

Table II. Solid-State Electronic Spectral Data[a]

Complex	Band max,[b] cm^{-1}
Co(3-CH_3OSALDAPE)	8330, 11 990
Co(5-CH_3OSALDAPE)	8470, 10 870
Co(5-ClSALDAPE)	6280, 14 490
Co(5-BrSALDAPE)	6280, 14 280
Co(3-NO_2SALDAPE)	6320, 13 000
Co(3-$CH(CH_3)_2$SALDAPS)	7800, 11 360, 17 700
Co(5-ClSALDAPS)	6090, 13 880
Co(5-BrSALDAPS)	6210, 14 080
Co(3-CH_3OSALPhDPT)	8190, 11 620
Co(5-CH_3OSALPhDPT)	7800,[c] 11 240
Co(5-ClSALPhDPT)	5900, 14 700
Co(SAL-*p*-ClPhDPT)	8330, 11 560, 17 300
Co(SAL-*p*-CH_3OPhDPT)	6310, 14 700
Co(SAL-*p*-CH_3PhDPT)	6300, 14 690
Co(3-NO_2SAL-*p*-ClPhDPT)	5810, 14 800

[a] Compounds were run as Nujol mulls. [b] Higher energy intense charge-transfer bands were also present. [c] This peak shows slight splitting.

visible–near-infrared spectrum of Co(SALPhDPT) is very similar to that of Co(SALDPT) and Co(SALMeDPT). These latter compounds were found to be isomorphous with the analogous nickel complexes which have structures intermediate between a trigonal bipyramid and a square pyramid.[11] Thus, it is assumed that Co(SALPhDPT) also has an intermediate five-coordinate structure. On the other hand, the spectra of Co(SALDAPE) and Co(SALDAPS) more closely resemble that of Co(SALHTDA), a four-coordinate complex containing a methylene carbon in place of a central donor (structure II, *n* = 7). We believed that the preference of Co(SALDAPE) and Co(SALDAPS) to be tetrahedral can be attributed to the very weak coordinating tendency of the central donor. Upon examining the electronic spectra of the *substituted* compounds, we were surprised to find that some of the ligand-substituted derivatives of Co(SALDAPE) and Co(SALDAPS) exhibited spectra similar to that of five-coordinate Co(SALPhDPT) (Figure 1), whereas some of the ligand-substituted derivatives of Co(SALPhDPT) exhibited visible–near-infrared spectra (Figure 2) similar to those of the tetrahedral Co(SALDAPE) and Co(SALDAPS) complexes.

In order to determine if these structural anomalies were the result of steric factors, various other compounds were prepared which differed in the placement of substituent groups at other positions on the ligands including the para position of PhDPT. Table II summarizes the solid-state electronic spectra of all compounds studied. Without exception, the complexes are either five-coordinate (absorptions at ca. 6000 and 14 000–15 000 cm^{-1}) or tetrahedral (absorptions at ca. 8000 and 11 000–12 000 cm^{-1}). In the case of the tetrahedral compounds, these bands have been assigned to low-symmetry components of the transition from the $^4A_2$ ground state to the $^4T_1(F)$ state. Most tetrahedral complexes also have bands in the 17 000–19 000-cm^{-1} region assigned to the $^4A_2$ to $^4T_1(P)$ transition. These are observed as shoulders in the unsubstituted compounds but were usually obscured by intense charge transfer or ligand–ligand transitions in the substituted complexes.

Table III. Substituent Effects: Coordination Number

R (electronic effect)	Co(RSAL-DAPS)	Co(RSAL-DAPE)
H	4	4
5-CH_3O (−*I*, +*M*)		4
3-CH_3O (−*I*, +*M*)		4
3-$CH(CH_3)_2$ (+*I*)	4	
3-NO_2 (−*I*, −*M*)		5
5-Br (−*I*, +*M*)	5	5
5-Cl (−*I*, +*M*)	5	5

Table IV. Substituent Effects: Coordination Number

R (electronic effect)	R′ (electronic effect)	Co(RSALR′-PhDPT)
H	H	5
5-CH_3O (−*I*, +*M*)	H	4
3-CH_3O (−*I*, +*M*)	H	4
5-Cl (−*I*, +*M*)	H	5
H	*p*-Cl (−*I*, +*M*)	4
H	*p*-CH_3O (−*I*, +*M*)	5
H	*p*-CH_3 (+*I*)	5
3-NO_2 (−*I*, −*M*)	*p*-Cl (−*I*, +*M*)	5

In some cases the complexes were recrystallized and the properties of the recrystallized materials were found to be the same as those from the direct synthesis. We can therefore assume that these results are not a phenomenon of the solution from which the compounds were prepared. Nor do we feel that a steric effect is responsible for these observations. Instead, we believe that an electronic effect is responsible for this unusual behavior. Tables III and IV correlate the coordination numbers of the complexes with the various substituents. Included in these tables is the resonance (±*M*) and inductive (±*I*) effect of each particular group. First, consider Table III which deals only with substitution on the salicylaldehyde portion of the ligand. For those substituents (5-CH_3O, 3-CH_3O, 3-$CH(CH_3)_2$) in which the overall effect is electron donating, only tetrahedral geometries are observed, whereas electron-withdrawing substituents (3-NO_2, 5-NO_2, 5-Cl, 5-Br) give rise to five-coordinate structures.

Considering any steric effect that might be present, it does not matter in which position (3 or 5) the group is placed, but only whether or not the overall effect is electron donating or electron withdrawing. Nevertheless, it should be noted that the 4 and 6 positions were not tested. Models indicate that sterically these positions offer no more interference than the 3 and 5 positions. However, electronically, the effect of substitution in these positions might be quite different. This is because in the 3 and 5 positions the electronic effect is operating through the phenolic donor. In the 4 and 6 positions, the maximum effect will be through the imine donor. If the structure of the five-coordinate complexes is similar to that of Co(SALDPT) and Co(SALMeDPT),[4] then the imine groups will be coordinated in the axial positions of the trigonal-bipyramidal structure. This is in contrast to the phenolic groups which occupy equatorial positions. This is important

Table V. Infrared Data (cm^{-1})

Compd	C-O-C	C=N
H_2(5-CH_3OSALDAPE)	1120	1650
Co(5-CH_3OSALDAPE)	1130	1615
H_2(5-BrSALDAPE)	1120	1640
Co(5-BrSALDAPE)	1070	1635
H_2(5-ClSALDAPE)	1120	1635
Co(5-ClSALDAPE)	1070	1635
H_2(3-NO_2SALDAPE)	1120	1645
Co(3-NO_2SALDAPE)	1070	1635
H_2(3-CH_3OSALDAPE)	1110	1630
Co(3-CH_3OSALDAPE)	1110	1605
H_2(5-BrSALDAPS)		1635
Co(5-BrSALDAPS)		1625
H_2(5-ClSALPhDPT)		1635
Co(5-ClSALPhDPT)		1635
H_2(5-CH_3OSALPhDPT)		1640
Co(5-CH_3OSALPhDPT)		1605

when it is considered that the central donor would also be coordinated equatorially. Thus, electronic effects acting through the phenolic linkage should have a greater influence on the coordination of the central donor.

This unusual effect can now be explained in the following way. Electron-donating groups increase electron density on the metal; consequently there is little tendency for the metal to expand its coordination sphere by bonding with a weak donor. On the other hand, electron-withdrawing groups decrease electron density on the metal thereby facilitating the coordination of the central donor which replenishes some of the lost electron density. In order to explain the apparent anomaly in the unsubstituted compounds, it is assumed that the phenylamine is a stronger donor than the ether oxygen or thioether sulfur. If the phenylamine were a weaker donor, it would be expected that the corresponding complex would be four-coordinate. This is accomplished by placing an electron-withdrawing group pàra to the nitrogen. Thus, Co(SAL-*p*-ClPhDPT) is tetrahedral (see Table IV). These results indicate that coordination of the central donor can be thought of in terms of a Lewis acid–base concept. Electron-withdrawing groups on the salicylaldehyde in essence cause cobalt to become a stronger Lewis acid. However, electron-withdrawing groups on the phenylamine decrease the Lewis basicity of the donor. A steric effect is ruled out here too since the *p*-CH_3 and *p*-CH_3O complexes are five-coordinate, as expected. The coordination of the *p*-ClPhDPT nitrogen should be accomplished by placing electron-withdrawing groups on the salicylaldehyde. When this is done, the resulting complex is five-coordinate.

The variation in structure with the variation in the donor strength of the phenylamine is proof that it is the central donor that is not coordinating in the four-coordinate complexes. Further evidence for this comes in the form of infrared data. Table V shows the ir data of some of the complexes and ligands. For the DAPE compounds, if the ether oxygen is coordinated, we would expect to observe in the complex a shift to lower frequency for the C–O–C asymmetric stretch. In some of the DAPE complexes, no shift is observed, but in others, shifts of 50 cm^{-1} to lower frequency are taken as evidence of coordination. The complexes which show this decrease in frequency are the same ones that give five-coordinate spectra. In trying to make the same comparisons with the other compounds, the C–S–C stretch was too weak to be observed and the phenylamine stretch was obscured by other peaks. Another trend was observed in the ir spectra concerning the C=N stretching mode. Although in most complexes this stretching frequency is reduced, the difference between the ligand and complex is much greater in the four-coordinate compounds. Whereas the five-coordinate complexes show 0–10-cm^{-1} shifts, the four-coordinate complexes show a 35-cm^{-1} shift.

Table VI. Electronic Absorption Data for Solution Spectra[a]

Complex	Molar concn	Band max, cm^{-1} (ϵ)[b]
Co(5-BrSALDAPS)	0.032	7350 (34.4), 11 700 (38.1), 17 200 (54.4)
	0.009	7350 (32.1), 11 700 (42.9), 17 200 (58.9)
Co(3-CH_3OSALPhDPT)	0.031	7460 (29.4), 11 900 (27.1), 17 860 (48.0)
	0.012	7460 (33.1), 11 900 (32.3), 17 860 (49.2)
Co(5-BrSALDAPE)	0.086	6580 (9.8), 13 520 (13.5)
	0.035	6580 (9.8), 13 520 (13.6)

[a] Obtained in chloroform. [b] Molar extinction coefficients.

Probably more surprising than the structural changes in the solid state were the structural changes in solution which were observed for two of the five-coordinate complexes. Co(5-ClSALDAPS) and Co(5-BrSALDAPS), although five-coordinate in the solid state, become tetrahedral in solution. At this point we were concerned that the five-coordinate geometry may be the result of some type of associated species, an intermolecular dimer which could dissociate in solution. Although models indicated a structure of this type was possible, electronic spectra at different concentrations and in solvents of varying polarity showed no trend which could be associated with an equilibrium mixture. For example, Table VI lists the electronic absorption data for three of the complexes in solution at two different concentrations. In comparing Co(5-BrSALDAPS) to Co(3-CH_3OSALPhDPT), there are essentially no differences in the peak maxima or extinction coefficients which are similar to those of other distorted tetrahedral complexes. The spectrum of the five-coordinate complex, Co(5-BrSALDAPE), is also independent of concentration. Furthermore, molecular weight measurements in chloroform on the complexes that remained five-coordinate in solution showed the compounds to be monomeric (Co(5-BrSALDAPE), (mol wt found)/(mol wt calcd) = 1.03; Co(5-ClSALPhDPT), (mol wt found)/(mol wt calcd) = 1.04). The similarity in the spectra of these five-coordinate complexes in solution with the solid-state spectra of Co(5-ClSALDAPS) and Co(5-BrSALDAPS) suggests they all have similar structures. This rules out a dimeric species since a different structural arrangement would probably be necessary. This would also seem to indicate that back-bonding is not taking place with the thioether as it is in the complex where the central donor is a phosphine.[6] If this is true, then the thioether sulfur may be the weakest σ donor, and in solution, solvation effects are able to override the coordination properties of this atom.

Conclusion

We have shown that structural changes can be imposed on a group of Co(II) complexes, simply by changing the substituents on the ligands. Since all the complexes were prepared in the same manner and since the position of the substituent is apparently unimportant, some other factor must be responsible for the observed changes. Grouping the substituents according to electron-donating and -withdrawing properties suggests that an electronic effect is responsible. The Schiff base ligands that give rise to this behavior are potentially pentadentate with a weak central donor. In other words, it is possible to enhance coordination of weak donors in complexes of this type simply by reducing the electron density on a transition metal. This could possibly be done by other means such as incorporating ligands with back-bonding or oxidative properties. We are currently investigating this last possibility. Preliminary results on the nickel(II) complexes of these ligands indicate that the same type of electronic effect may also be operating.

Acknowledgment. We wish to thank S. R. Edmonson for first preparing Co(5-BrSALDAPS) and Co(5-BrSALDAPE); we also thank A. K. St. Clair for her preparation of Co(3-$\mathrm{CH(CH_3)_2}$SALDAPS). This research is supported by the Research Corp.

Registry No. Co(3-$\mathrm{CH_3}$OSALDAPE), 59831-25-3; Co(5-$\mathrm{CH_3}$OSALDAPE), 59831-26-4; Co(5-ClSALDAPE), 59831-27-5; Co(5-BrSALDAPE), 59831-28-6; Co(3-$\mathrm{NO_2}$SALDAPE), 59831-29-7; Co(3-$\mathrm{CH(CH_3)_2}$SALDAPS), 59831-30-0; Co(5-ClSALDAPS), 59831-31-1; Co(5-BrSALDAPS), 59831-32-2; Co(3-$\mathrm{CH_3}$OSALPhDPT), 59831-33-3; Co(5-$\mathrm{CH_3}$OSALPhDPT), 59831-34-4; Co(5-ClSALPhDPT), 59831-35-5; Co(SAL-*p*-ClPhDPT), 59831-36-6; Co(SAL-*p*-$\mathrm{CH_3}$OPhDPT), 59831-37-7; Co(SAL-*p*-$\mathrm{CH_3}$PhDPT), 59831-38-8; Co(3-$\mathrm{NO_2}$SAL-*p*-ClPhDPT), 59831-39-9.

References and Notes

(1) Presented in part at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., 1975; taken from the Ph.D. thesis of R. H. Niswander, Virginia Polytechnic Institute and State University, 1976.

(2) (a) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Prog. Inorg. Chem.*, **7**, 83 (1966); (b) L. Sacconi, *Transition Met. Chem.*, **4**, 272 (1968).

(3) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969).

(4) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

(5) S. R. Edmondson, W. M. Coleman, and L. T. Taylor, *Inorg. Chem.*, **12**, 1191 (1973).

(6) R. H. Niswander, A. K. St. Clair, S. R. Edmondson, and L. T. Taylor, *Inorg. Chem.*, **14**, 478 (1975).

(7) J. C. Duff, *J. Chem. Soc.*, 547 (1941).

(8) M. Israel, J. S. Rosenfield, and E. J. Modest, *J. Med. Chem.*, **7**, 710 (1964).

(9) S. Gabriel and W. E. Laver, *Ber. Dtsch. Chem. Ges.*, **23**, 88 (1890).

(10) J. T. Braunholtz and F. C. Mann, *J. Chem. Soc.* 1817 (1953).

(11) M. DiVaira, P. L. Orioli, and L. Sacconi, *Inorg. Chem.*, **10**, 553 (1971).

(12) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **10**, 2667 (1971).

Contribution from the Lash Miller Chemical Laboratories,
University of Toronto, Toronto, Ontario

Conformational Dissymmetry. Conformational Isomers of Bis((*R*,*S*)-2,4-pentanediamine) Complexes

HEATHER BOUCHER and B. BOSNICH*

Received March 22, 1976 AIC60206I

The five possible conformational isomers of the ion $[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{X}_2]^+$ (R,S-dmtn = *meso*-2,4-pentanediamine), three cis and two trans isomers, have been prepared by a variety of kinetic and thermodynamic methods. All were isolated and characterized. It was found that unique and exclusive stereochemical relationships obtain in transferring from the cis to trans isomers, the isomerism of the trans complex being determined by that of the cis isomer from which it is derived. Under appropriately controlled conditions, the converse is true. The mechanistic implication of these observations is discussed. The equilibrium constant for the three *cis*-diaquo isomers has been determined.

Conformational calculations predict[1-3] and experimental studies confirm[4-9] that the isolated trimethylenediamine (tn) chelate ring prefers the chair conformation over any of the other possible conformations. This preference is further reinforced in the analogous dimethyl-substituted ligand, *meso*-2,4-pentanediamine (*R*,*S*-dmtn), where the chair chelate ring is stabilized by the requirement that the methyl groups are equatorially disposed. When two or more of either of these ligands is coordinated to a metal atom, the similarity between them diverges; the tn ligand is capable of inverting its chair rings and seeking the most stable relationship between adjacent rings, whereas the *R*,*S*-dmtn ligand locks a particular chair conformation so that, for a system containing two or more of these rings, particular isomers arise because of the fixed relationships between the rings.

This paper describes the isolation of all (five) possible conformational isomers of the $[\mathrm{M}(R,S\text{-dmtn})_2\mathrm{X}_2]^{n+}$ system in pure crystalline forms. In order to achieve this, we have resorted to both thermodynamic and kinetic means. The kinetically based separations, we believe, are of considerable general importance for they imply a uniqueness about substitution and stereochemical rearrangement in octahedral systems.

I. Isomers

Figure 1 shows the five possible isomers of the octahedral $[\mathrm{M}(R,S\text{-dmtn})_2\mathrm{X}_2]^{n+}$ system, two trans and three cis isomers. We refer to the two trans as *trans*-(C_{2v}) and *trans*-(C_{2h}) and the three cis isomers as *cis*-(C_2)-*anti*, *cis*-(C_2)-*syn*, and *cis*-(C_1). The syn and anti designations specify whether the two chelate rings both fold toward each other (syn) or both fold away from each other (anti); the *cis*-(C_1) has the rings folding in–out. We should point out that these isomers arise primarily because of the relative orientations of the (*R* or *S*) chiral centers of the ligands (Figure 1) and the fixed chair conformations are a secondary assumption although it is almost certainly correct. For example, *meso*-2,3-butanediamine would give the same number of isomers.

Of the two trans isomers the steplike *trans*-(C_{2h}) configuration is probably more stable. This is suggested by the determined crystal structures of *trans*-$[\mathrm{M(tn)_2X_2}]^{n+}$ systems,[6,7,9] all of which have the *trans*-(C_{2h}) arrangement. The *cis*-(C_2)-*syn* isomer is undoubtedly less stable than the other two because of steric crowding,[10] but the other two may be of comparable energy. Thus the crystal structure of *cis*-$[\mathrm{Co(tn)_2(NCS)_2}][\mathrm{Sb((+)\text{-}tart)}]\cdot 2\mathrm{H_2O}$[8] reveals the chair tn rings in a *cis*-(C_2)-*anti* configuration whereas the $[\mathrm{Co(tn)_2CO_3}]\mathrm{ClO_4}$ crystal structure has the tn rings in essentially chair conformations but in a *cis*-(C_1) configuration.[10]

II. Mechanism

The most intriguing aspect of this system is that it potentially provides a fine stereochemical probe into the mechanisms of stereochemical change in octahedral systems. In order to focus on this possibility, we assume that the elementary act by which one isomer interconverts to another is an edge displacement of one donor nitrogen atom to an adjacent cis position. In Figure 2 we show an interconversion scheme for the five isomers; in going from one isomer to another, only one edge displacement is invoked. Only a selected number of edge displacements are shown; these are sufficient to illustrate the basic features of the system.