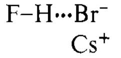
by adding HF to the F_2 used in a final CsBr experiment which also revealed a strong, broad 2805-cm^{-1} absorption in addition to the sharp 849- and 744-cm^{-1} absorptions.

Assignment of the absorptions in Table IV to bihalide species is confirmed by recent salt reactions with HF and DF performed by Ault.[12] The interesting question remaining is the type of bihalide species responsible for the Table IV absorptions. The original observation of $F-H\cdots Br^-$ species by Evans and Lo[13] revealed a very strong, broad perturbed H–F stretching mode at 2900 cm^{-1} and a sharp bending mode at 740 cm^{-1}. Clearly the present 2805 and 744 cm^{-1} argon matrix absorptions are due to the type I hydrogen-bonded complex



$$\underset{Cs^+}{F-H\cdots Br^-}$$

The sharp 849-cm^{-1} band could be another bending mode of the linear $F-H\cdots Br^-$ ion since the Cs^+ ion will remove the degeneracy of the bending mode for the linear molecule. The relative intensities of the 2805-, 849-, and 744-cm^{-1} absorptions are constant in the present experiments and in the HF + CsBr and HBr + CsF work of Ault.[12] On the other hand, a type II hydrogen bonded species with two weak hydrogen–halide bonds, $F\cdots H\cdots Br^-$, could also be formed and stabilized by the cation, as mentioned previously, and it could reasonably be expected to exhibit an "antisymmetric" hydrogen stretching mode in this region. Studies of the isolated mixed ions in this laboratory revealed a weak 2761-cm^{-1} band for $F-H\cdots Cl^-$ and a weak 2961-cm^{-1} absorption for $F-H\cdots Br^-$, both type I species, without new product absorptions in the 700–1000-cm^{-1} region.[14] This suggests that a bound cation is required to stabilize a type II mixed bihalide ion.

Conclusions

The cocondensation reaction of alkali bromide and iodide salt molecules with argon/fluorine mixtures has produced new infrared absorptions which are assigned to the mixed trihalide species FXF^- and XFF^-. The new absorption in the 500-cm^{-1} region attributed to the antisymmetric X–F stretching mode of the former shows considerable heavy halogen shift whereas the product in the higher 300-cm^{-1} region attributed to the F–F mode of the latter exhibits little halogen shift. The observation of alkali fluoride and XF products provides the overall reaction mechanism $MX + F_2 \rightarrow M^+XFF^- \rightarrow M^+FXF^- \rightarrow MF + XF$. Salt reactions with HF impurity also produced the bihalide species M^+FHX^-.

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Registry No. Na^+FClF^-, 62624-99-1; K^+FClF^-, 15321-05-8; Na^+FBrF^-, 69204-01-9; K^+FBrF^-, 69204-02-0; Rb^+FBrF^-, 69204-03-1; Cs^+FBrF^-, 40419-00-9; Na^+FIF^-, 69204-05-3; K^+FIF^-, 69204-06-4; Rb^+FIF^-, 69204-07-5; Cs^+FIF^-, 69204-08-6; K^+ClFF^-, 69204-09-7; K^+BrFF^-, 69204-10-0; Rb^+BrFF^-, 69204-11-1; Cs^+BrFF^-, 69204-12-2; K^+IFF^-, 69204-13-3; Rb^+IFF^-, 69204-14-4; Cs^+IFF^-, 69204-15-5; Na^+FHCl^-, 69204-16-6; Na^+FHBr^-, 69204-17-7; Na^+FHI^-, 69204-18-8; K^+FHCl^-, 69204-19-9; K^+FHBr^-, 69204-20-2; K^+FHI^-, 69204-21-3; Rb^+FHCl^-, 69204-22-4; Rb^+FHBr^-, 69204-23-5; Rb^+FHI^-, 69204-24-6; Cs^+FHCl^-, 69204-25-7; Cs^+FHBr^-, 69204-26-8; Cs^+FHI^-, 69204-27-9; CsF, 13400-13-0; $Cs^+F_3^-$, 58915-74-5; BrF, 13863-59-7; IF, 13873-84-2.

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Magnetic and Spectral Properties of Oxovanadium(IV) Complexes of ONO Donor Tridentate, Dibasic Schiff Bases Derived from Salicylaldehyde or Substituted Salicylaldehyde and *o*-Hydroxybenzylamine

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The oxovanadium(IV) complexes of Schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 4-methoxysalicylaldehyde, 3,5-dichlorosalicylaldehyde, 2-hydroxy-1-naphthaldehyde, and *o*-hydroxybenzylamine are synthesized and characterized by elemental analysis, infrared and electronic spectra, and magnetic susceptibility measurements from 80 to 294 K. The Schiff bases behave as tridentate, dibasic ONO donor ligands. The complexes exhibit subnormal magnetic moments (μ_{eff} = 1.10–1.23 μ_B at room temperature). The magnetic moments of the complexes decrease significantly as the temperature is lowered indicating the presence of antiferromagnetic exchange with a singlet ground state. The exchange interaction parameter, J, of the complexes is in the range −241 to −307 cm^{-1}. The complexes exhibit three electronic spectral bands at around 13 000, 18 000, and 23 000 cm^{-1} due to the transitions $d_{xy} \rightarrow d_{xz}, d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{z^2}$, respectively. The ν(V=O) frequency of the complexes is observed in the region 900–910 cm^{-1}. On the basis of magnetic susceptibility and infrared data, a dimeric structure with benzylaminophenol oxygen atoms as the bridging atoms is suggested.

Introduction

There has been considerable interest in the structural, magnetic, and spectral properties of metal(II) and -(III) complexes with tridentate, dibasic ligands in recent years.[1-4] These ligands force the metal(II) and -(III) ions to dimerize or polymerize leading to metal complexes with unusual magnetic and structural properties. Oxovanadium(IV) complexes with tridentate, dibasic Schiff bases (I) with subnormal magnetic moments have been reported, and the

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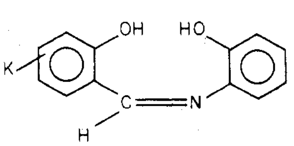

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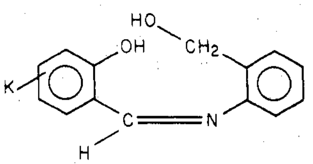

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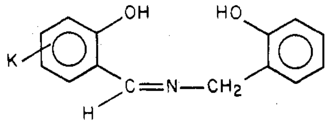


III

authors have suggested a dimeric structure with aminophenol oxygen atoms as the bridging atoms.[5] We have recently described[6] the synthesis of oxovanadium(IV) complexes of tridentate, dibasic Schiff bases (II) and these complexes also possess subnormal magnetic moments. A dimeric structure with aminobenzyl alcohol oxygen atoms as the bridging atoms has been suggested.[6] The Schiff bases II and III are isomeric, and in II and III the CH_2 group occurs at a different position. We think it is of interest to see the effect of the CH_2 group at different positions on the magnetic properties of the oxovanadium(IV) complexes of II and III. Furthermore, the basic structure of *N*-alkylsalicylaldimines embodies several key molecular features common to pyridoxal-mediated reactions, and as such salicylaldimines are chemical prototypes of pyridoxal and in general the B_6 vitamins. Thus the study of metal complexes of *N*-alkylsalicylaldimines is of biochemical interest. We report in this paper the synthesis of new oxovanadium(IV) complexes of III. We have characterized the complexes on the basis of elemental analysis, magnetic susceptibility measurements (80–294 K), and infrared and electronic spectra. A comparison of the magnetic properties of oxovanadium(IV) complexes of I, II, and III is presented.

Experimental Section

Materials and Methods. Oxovanadium(IV) dichloride dihydrate was obtained from K and K Laboratories Inc. Salicylaldehyde was of Sarabhai M. Co. reagent grade material. 5-Chlorosalicylaldehyde was prepared in the laboratory according to the published procedure.[7] 2-Hydroxy-1-naphthaldehyde was purchased from Fluka AG. 5-Bromosalicylaldehyde and 4-methoxysalicylaldehyde were the products of Aldrich Chemical Co. 3,5-Dichlorosalicylaldehyde was purchased from Eastman Kodak Co. *o*-Hydroxybenzylamine was prepared according to the published procedure.[8]

The vanadium content was determined gravimetrically as V_2O_5 after decomposing the complexes with concentrated nitric acid and then igniting. Carbon, hydrogen, and nitrogen analyses were done by the microanalytical services of Ciba-Geigy Research Centre, Bombay. The infrared spectra were recorded in KBr pellets by use of a Beckman IR 20 infrared spectrophotometer. The reflectance spectra were recorded on a Beckman DU recording spectrophotometer with a reflectance attachment. The magnetic measurements were carried out in the range 80–294 K by use of a Gouy balance fitted with a modified cryostat similar in design to that described in the literature.[9] Mercury tetrathiocyanatocobaltate(II) was used as the standard. The magnetic susceptibilities were corrected for the temperature-independent paramagnetism term[5] (50×10^{-6} cgsu) and the diamagnetic contribution of the metal–ligand system.[10] The magnetic data were computed on an Electronic Corporation of India Ltd. 360 computer. The experimental susceptibility data were fitted to the Bleaney–Bowers equation[11]

$$\chi_M = \frac{g^2 N \beta^2}{3kT}\,[1 + \tfrac{1}{3}\exp(-J/kT)]^{-1} + N_\alpha$$

(where g is the gyromagnetic ratio, χ_M is the magnetic susceptibility per g-atom of vanadium and N_α is the temperature-independent paramagnetism term estimated to be 50×10^{-6} csgu) employing a nonlinear least-squares fitting program utilizing $R = [(\sum(\chi_{obsd} - \chi_{calcd})^2)/\sum\chi_{obsd}^2]^{1/2}$ as fitting criterion.

General Method of Synthesis of the Complexes. Salicylaldehyde or substituted salicylaldehyde (0.005 mol) and *o*-hydroxybenzylamine (0.61 g, 0.005 mol) were refluxed in 50–70 mL of methanol for 30 min, and a yellow solution of the condensed Schiff base was obtained. To a methanolic solution of oxovanadium(IV) dichloride dihydrate (0.87 g, 0.005 mol in 20 mL) was added anhydrous sodium acetate (0.82 g, 0.01 mol), and the mixture was filtered off. To the filtrate containing the oxovanadium(IV) acetate was added slowly the Schiff-base solution with stirring, and the mixture was refluxed for 2 hr while being stirred magnetically. The separated greenish yellow precipitates were suction filtered, washed with methanol, and dried under vacuum at room temperature; yield 55%. The complexes are insoluble in water and common noncoordinating solvents. The analytical data are given in Table I.

Results and Discussion

The analytical data of the complexes indicate 1:1 metal:ligand stoichiometry, and hence the Schiff bases act as tridentate, dibasic ligands. In the infrared spectra of the ligands, a medium-intensity band at around 2700 cm^{-1} may be assigned to the intramolecularly hydrogen bonded ν(O–H) stretch. In the infrared spectra of the oxovanadium(IV) complexes, the absence of the ν(O–H) frequency indicates the deprotonation of both the replaceable hydrogen atoms and the dibasic character of the Schiff bases. The complexes are of the VOL type and are apparently four-coordinated. Hence they must be involved in bridges in order to satisfy the coordination number demands of the metal ions. The high melting or decomposition temperature (>250 °C) and the insolubility of the complexes in common noncoordinating solvents give an indication of dimeric or polymeric nature of the complexes. This is also supported by the magnetic susceptibility data (to be discussed later) of the complexes. The V=O frequency of the complexes (see Table II) occurs in the region 900–910 cm^{-1}, and this is close to the usual range (960 ± 50 cm^{-1}) observed for the majority of oxovanadium(IV) complexes.[12] In oxovanadium(IV) complexes with a ···V=O···V=O··· interaction, the ν(V=O) frequency occurs at a much lower wavenumber (~850 cm^{-1}).[13] The observation of the ν(V=O) stretch close to the normal range in our complexes argues against the presence of a ···V=O···V=O··· chain structure. Infrared spectral data have been used to predict the nature of the bridging oxygen atoms in the polymetallic complexes. A shift of the ν(C–O) stretch near 1540 cm^{-1} to higher frequency by 10–20 cm^{-1} has been unambiguously used to indicate the formation of a phenolic oxygen bridge in polymetallic complexes.[14] We have also observed such a shift of the ν(C–O) stretch to higher energy in the present complexes (see Table II), and this is indicative of the presence of a phenolic oxygen bridge. However, we find that the ν(C–O) stretch in some of the ligands occurs at around 1500 cm^{-1} (see Table II). The structure of III indicates that there are two phenolic oxygen atoms, (one is the phenolic oxygen atom of the benzylaminophenol part of the molecule and the other is the phenolic oxygen atom of the salicylaldehyde part of the molecule) which may be involved to form the M–O–M bridge. Infrared spectral data are unable to distinguish between these two possibilities. We suggest the presence of benzylaminophenol oxygen atoms as the bridging atoms similar to the aminophenol oxygen atoms acting as the bridging atoms in oxovanadium(IV) complexes of I.[5] The ν(C=N) stretch in the ligands was observed in the region 1630–1660 cm^{-1}. This band (see Table II) occurs in the oxovanadium(IV) complexes at lower frequency (10–40 cm^{-1}) indicating the nitrogen coordination of azomethine group of the ligands. The other salient feature in the infrared spectra of the complexes is the presence of a strong band around 1600 cm^{-1} assignable to ν(C=C) vibration.

The magnetic susceptibility data of the complexes in the range 80–294 K are given in Table III. The oxovanadium(IV)

Table I. Analytical Data of Oxovanadium(IV) Complexes of Tridentate Schiff Bases[a]

		% calcd				% found			
complex	stoichiometry	C	H	N	V	C	H	N	V
VO(sal-*o*-hydroxybenzylamine)	$VC_{14}H_{11}NO_3$	57.53	3.77	4.79	17.47	57.83	3.95	4.44	17.09
VO(5-chlorosal-*o*-hydroxybenzylamine)	$VC_{14}H_{10}NO_3Cl$	51.45	3.06	4.29	15.63	51.73	3.28	4.06	14.86
VO(5-bromosal-*o*-hydroxybenzylamine)	$VC_{14}H_{10}NO_3Br$	45.28	2.69	3.77	13.75	45.22	2.95	3.87	13.45
VO(4-methoxysal-*o*-hydroxybenzylamine)	$VC_{15}H_{13}NO_4$	55.90	4.04	4.35	15.84	55.34	4.33	4.11	15.38
VO(3,5-dichlorosal-*o*-hydroxybenzylamine)	$VC_{14}H_9NO_3Cl_2$	46.54	2.49	3.88	14.13	46.43	2.72	3.46	14.09
VO(hydrox-*o*-hydroxybenzylamine)	$VC_{18}H_{13}NO_3$	63.17	3.80	4.09	14.91	63.02	4.09	3.79	14.50

[a] Abbreviations: sal = salicylaldehyde, 5-chlorosal = 5-chlorosalicylaldehyde, 5-bromosal = 5-bromosalicylaldehyde, 4-methoxysal = 4-methoxysalicylaldehyde, 3,5-dichlorosal = 3,5-dichlorosalicylaldehyde, and hydrox = 2-hydroxy-1-naphthaldehyde.

Table II. Infrared and Electronic Spectral Data of Oxovanadium(IV) Complexes of Tridentate Schiff Bases[a]

	ν(C=N)		ν(C–O)			
complex	complex	ligand	complex	ligand	ν(V=O)	ν_{max}
VO(sal-*o*-hydroxybenzylamine)	1630	1657	1540	1530	910	13 200 sh, 19 700 sh, 24 000
VO(5-chlorosal-*o*-hydroxybenzylamine)	1625	1660	1530	1515	900	13 200 sh, 18 300 sh, 24 000
VO(5-bromosal-*o*-hydroxybenzylamine)	1635	1655	1530	1515	910	13 400 sh, 19 300 sh, 24 700
VO(4-methoxysal-*o*-hydroxybenzylamine)	1615	1660	1540	1525	910	13 300 sh, 18 700 sh, 24 600
VO(3,5-dichlorosal-*o*-hydroxybenzylamine)	1630	1640	1530	1500	900	12 200 sh, 18 200 sh, 23 000
VO(hydrox-*o*-hydroxybenzylamine)	1620	1630	1550	1530	910	13 200 sh, 18 000 sh, 23 000

[a] Values in cm^{-1}. See Table I for abbreviations.

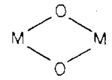
Table III. Magnetic Susceptibility and Magnetic Moment Data for Oxovanadium(IV) Complexes at 80–294 K[a,c]

VO(sal-*o*-hydroxybenzylamine)			VO(5-chlorosal-*o*-hydroxybenzylamine)			VO(5-bromosal-*o*-hydroxybenzylamine)		
temp, K	χ_M^{cor}, cgsu × 10^{-6}	μ_{eff}, μ_B	temp, K	χ_M^{cor}, cgsu × 10^{-6}	μ_{eff}, μ_B	temp, K	χ_M^{cor}, cgsu × 10^{-6}	μ_{eff}, μ_B
294	521	1.11	292	601	1.19	294	589	1.18
201	443	0.84	192	526	0.90	191	525	0.90
141	430	0.70 ($J = 298\ cm^{-1}$)[b]	139	459	0.72 ($J = 266\ cm^{-1}$)[b]	141	435	0.70 ($J = 264\ cm^{-1}$)[b]
114	359	0.57	111	418	0.61	114	463	0.65
99	367	0.54	98	452	0.60	99	510	0.64
87	354	0.50	80	457	0.54	86	564	0.62

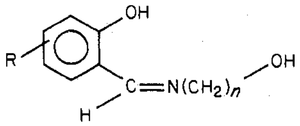
VO(4-methoxysal-*o*-hydroxybenzylamine)			VO(3,5-dichlorosal-*o*-hydroxybenzylamine)			VO(hydrox-*o*-hydroxybenzylamine)		
temp, K	χ_M^{cor}, cgsu × 10^{-6}	μ_{eff}, μ_B	temp, K	χ_M^{cor}, cgsu × 10^{-6}	μ_{eff}, μ_B	temp, K	χ_M^{cor}, cgsu × 10^{-6}	μ_{eff}, μ_B
292	641	1.23	291	525	1.11	293	508	1.10
191	523	0.90	193	441	0.83	191	432	0.82
138	467	0.72 ($J = 241\ cm^{-1}$)[b]	139	363	0.64 ($J = 307\ cm^{-1}$)[b]	139	465	0.72 ($J = 274\ cm^{-1}$)[b]
111	546	0.70	113	337	0.55	84	583	0.63
97	602	0.69	98	343	0.52			
83	627	0.65	86	341	0.49			

[a] The magnetic moment was calculated with the Curie equation: $\mu_{eff} = 2.84(\chi_M^{cor}T)^{1/2}\ \mu_B$. [b] $g = 1.99$, TIP = 50×10^{-6} cgsu. [c] See Table I for abbreviations.

ion belongs to the $S = {}^1/_2$ system, and magnetically dilute oxovanadium(IV) complexes should exhibit magnetic moments very close to the spin-only moment of 1.73 μ_B as the spin–orbit coupling constant (λ) is positive for and the orbital contribution is almost completely quenched in oxovanadium(IV) complexes.[15,16] The room-temperature magnetic moments (1.10–1.23 μ_B) of the complexes are remarkably less than the spin-only moment, and this is indicative of the presence of strong antiferromagnetic exchange. The magnetic moments of the complexes decrease significantly as the temperature is lowered, and this confirms the presence of antiferromagnetic exchange interaction of the neighboring VO^{2+}–VO^{2+} ions. The ground state in these magnetically condensed complexes is $S = 0$. The complexes do not exhibit any dependence on the magnetic field strength, and this is indicative of the absence of ferromagnetic exchange. The singlet–triplet splitting parameter, J, of the complexes is in the range –241 to –307 cm^{-1} indicating the presence of strong antiferromagnetic exchange interaction. On the basis of magnetic and infrared data, a dimeric structure with benzylaminophenol oxygen atoms as the bridging atoms is suggested for these oxovanadium(IV) complexes.[5] The J values are similar in these complexes indicating the similarity of the structure of these complexes. The J values of the oxovanadium(IV) complexes of III do not change appreciably with the variation of substituents at 4; 5; 3, 5; and 5, 6 positions of salicyaldehyde part of the molecules. This reflects that the substituents in the salicylaldehyde part of the molecules have very little effect on the bridging benzylaminophenol oxygen atoms. The electronic effect of substitution in oxovanadium(IV) complexes is relatively unimportant except for any structural modifications they produce in the



bridge via alteration of molecular packing.[4] The J values of the oxovanadium(IV) complexes of III are higher than those of the oxovanadium(IV) complexes of II. The size of the chelate ring is six-membered in the oxovanadium(IV) complexes of both the Schiff bases II and III in the aminobenzyl alcohol or aminophenol part of the molecules. The CH_2 groups are very close to the bridging enolic oxygen atoms in the oxovanadium(IV) complexes of II but are far away from the bridging phenolic oxygen atoms in the oxovanadium(IV) complexes of III. The presence of the CH_2 groups close to the bridging oxygen atoms in the oxovanadium(IV) complexes of II would lead to a longer V–V distance due to steric influence; hence the magnetic interaction will be weaker in oxovanadium(IV) complexes of II than in those of III. Furthermore, the delocalization of the vanadium(IV) electrons will be more effective in complexes of III in comparison to the complexes of II due to the difference in position of the CH_2 group. The magnetic data of the oxovanadium(IV) complexes of II and III preclude the possibility of bridging through the phenolic oxygen atoms of salicylaldehyde part of the molecule. If phenolic oxygen atoms of the salicylaldehyde moiety are involved in the bridging, then *J* should not vary in these two series of complexes since the electronic environment in the chelate ring is the same. In oxovanadium(IV) complexes of IV ($n = 2$), the magnetic exchange interaction has been found to be of greater magnitude than in the oxovanadium(IV) complexes of IV ($n = 3$).[17] This has been explained on the basis of the chelate ring effect; the magnetic interaction is greater in the case of a five-membered chelate ring ($n = 2$ complexes) than in the case of a six-membered chelate ring ($n = 3$ complexes) in the amino alcohol part of the molecules. As the oxovanadium(IV) complex of III has greater magnetic-exchange interaction than that of I, it is apparent that the chelate ring effect is not operative in these systems with more aromatic character and more steric rigidity (cf. less aromatic character and less steric rigidity in oxovanadium(IV) complexes of IV).



IV: $n = 2$ or 3

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Registry No. VO(sal-*o*-hydroxybenzylamine), 69204-55-3; VO(5-chlorosal-*o*-hydroxybenzylamine), 69204-54-2; VO(5-bromosal-*o*-hydroxybenzylamine), 69204-53-1; VO(4-methoxysal-*o*-hydroxybenzylamine), 69204-52-0; VO(3,5-dichlorosal-*o*-hydroxybenzylamine), 69204-51-9; VO(hydrox-*o*-hydroxybenzylamine), 69204-50-8; sal, 90-02-8; 5-chlorosal, 635-93-8; 5-bromosal, 1761-61-1; 4-methoxysal, 673-22-3; 3,5-dichlorosal, 90-60-8; hydrox, 708-06-5; *o*-hydroxybenzylamine, 932-30-9; oxovanadium(IV) dichloride, 10213-09-9.

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Electron Paramagnetic Resonance Investigation of Copper(II) Complexes with Reversed *g* Values in A and Y Zeolites

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The electron paramagnetic resonance (EPR) spectra of evacuated low ion exchanged copper(II) Y and A zeolites are presented, in which reversed *g* values are observed. The EPR parameters for CuY-10 and CuA-6 are $g_\perp = 2.32$ with $g_\parallel = 2.00$ (102) and $g_\perp = 2.30$ with $g_\parallel = 1.99$ (85), respectively, where the numbers in parentheses are the hyperfine splitting values (in gauss). It is proposed that these reversed spectra are due to pentacoordinated copper(II) ions held in the trigonal sodalite cage windows with water molecules in the axial positions to yield trigonal-bipyramidal complexes. Using a reoxidation technique, a similar diammine complex has been formed, which has EPR parameters of $g_\perp = 2.32$ and $g_\parallel = 1.97$ (131). The latter values are similar to those previously reported for an amminecopper(II) complex formed by an evacuation procedure. Only part of the divalent copper in the zeolites form the bipyramidal complexes that are decomposed by thermal treatments.

Introduction

Synthetic zeolites, such as A, L, X, and Y, have rigid three-dimensional lattices that provide interesting media in which to study the coordination chemistry of transition-metal ions. The exchangeable cations can be located in a number of coordination sites in the dehydrated zeolites, where they are usually coordinatively unsaturated. This results in the ready reactivity of the cations toward a wide range of ligands (L) to form complexes ranging from lattice-held ML to free ML_6 complexes located in the supercages.

Zeolite A is structurally fairly simple and the cation-exchanged forms of this zeolite have been the most extensively

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