Magnetic Properties of Some *N*-(2-Hydroxyphenyl)-2-hydroxy-1-naphthylmethyleneiminato-complexes of the Oxovanadium(IV) Ion

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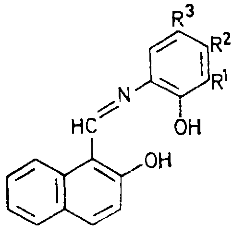
The magnetic properties of a number of oxovanadium(IV) complexes of general formula [VO(L)],*n*X (L = a Schiff's base ligand derived from 2-hydroxy-1-naphthaldehyde and one of a number of substituted 2-aminophenols, X = solvent molecule, and *n* = 0 or 1) have been investigated over the temperature range 77—300 K. The solvated complexes (*n* = 1, X = H_2O or EtOH) obey the Curie–Weiss law, but the other complexes (*n* = 0) exhibit antiferromagnetic behaviour. The experimental data for the antiferromagnetic complexes indicate polymetallic structures and have been interpreted by use of the spin–spin exchange theory assuming both dimetallic and infinite linear-chain models.

OXOVANADIUM(IV) (d^1) and copper(II) (d^9) ions resemble each other magnetically in that each has a single unpaired electron. However, the symmetries of the unpaired electrons are quite different, that in copper(II) being derived from the e_g set, whereas the electron in oxovanadium(IV) ion is derived from the t_{2g} set. A rather large number of copper(II) complexes with subnormal magnetic moments are known[1,2] and are a source of continuing interest and controversy. The majority of oxovanadium(IV) complexes investigated thus far are paramagnetic with magnetic moments corresponding to the theoretical spin-only value for one unpaired electron. The temperature dependence of their magnetic susceptibilities generally obeys the Curie–Weiss law. Only a few examples of magnetically condensed oxovanadium(IV) complexes have been reported.[3–7] We are currently investigating magnetic exchange in transition-metal complexes derived from Schiff's bases, and here report the magnetic properties of oxovanadium(IV) complexes of *N*-(2-hydroxyphenyl)-2-hydroxy-1-napthylmethyleneimines, (I)—(VI).



(I); $R^1 = R^2 = H, R^3 = NO_2$
(II); $R^1 = R^3 = NO_2, R^2 = H$
(III); $R^1 = R^2 = H, R^3 = Cl$
(IV); $R^1 = R^3 = H, R^2 = NO_2$
(V); $R^1 = R^2 = H, R^3 = Ph$
(VI); $R^1 = R^2 = R^3 = H$

EXPERIMENTAL

The complexes were prepared as described previously.[8] Magnetic susceptibilities were determined by the Faraday method over the temperature range 77—300 K. The cryomagnetic equipment was very similar to that of Hatfield *et al.*[9] Magnetic-field strengths were calibrated with mercury(II) tetrathiocyanatocobaltate(II)[10] and diamagnetic corrections were estimated by using Pascal's constants.[11] The experimental results are listed in the Table. Parameters such as *g*, *J*, *N*α, and θ were determined from best fits of the experimental data to appropriate magnetic susceptibility equations as described below. A negative value of θ refers to a negative intercept on the temperature axis.

RESULTS AND DISCUSSION

Magnetic susceptibilities and detailed results are given in the Table. Two of the complexes, [VO(L)],*n*X [L = (I), X = EtOH, *n* = 1; L = (II), X = H_2O, *n* = 1], appear to be magnetically dilute as their data obey the Curie–Weiss equation (1):

$$\chi_M^{corr} = \frac{Ng^2\beta^2}{3k(T-\theta)} S(S+1) + N\alpha \qquad (1)$$

We suggest that these two complexes are five-co-ordinate monomers in which a solvent molecule occupies one of the co-ordination positions. Analogous structures have been proposed for paramagnetic monosolvated oxovanadium(IV)[5] and copper(II)[12] complexes with tridentate Schiff's bases. Both our complexes have a single VO stretching frequency in the normal range for ν(V=O). The magnetic moments for the complexes are very close to the spin-only value and fall within the range usually expected for paramagnetic oxovanadium(IV) complexes. However, polymetallic structures can not be ruled out completely since very weak magnetic interactions could be present and yet not be observed for the temperature range investigated.

Effective magnetic moments for the complexes [VO(L)] (L = (III)—(V)] are considerably lower than the spin-only value of 1·73 B.M. This reduction of magnetic moments and the curvature in plots of $1/\chi_M^{corr}$

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against T indicate the presence of antiferromagnetic spin-exchange interactions resulting from a polymetallic structure. Therefore the experimental susceptibilities were compared with the theoretical expressions for chain arrangements of interacting spins, by use of a least-squares-fitting computer program. The data were best-fit to magnetic-susceptibility equations (2)—(4) for an infinite linear chain of Ising spins,[13] where $K =$

$$\langle\chi\rangle = \tfrac{1}{3}\chi_{\parallel} + \tfrac{2}{3}\chi_{\perp} + N\alpha \qquad (2)$$

$$\chi_{\parallel} = Ng^2\beta^2Ke^{2K}/4|J| \qquad (3)$$

$$\chi_{\perp} = Ng^2\beta^2\,(\tanh|K| + |K|\operatorname{sech}^2K)/8|J| \qquad (4)$$

$J/\boldsymbol{k}T$. However, reasonably good fits could also be obtained by using the susceptibility equation (5)[14] for exchange-coupled pairs, where χ_A' is the susceptibility

$$\chi_A' = \frac{Ng^2\beta^2}{3\boldsymbol{k}T}\,[1 + \tfrac{1}{3}\exp{(2J/\boldsymbol{k}T)}]^{-1} + N\alpha \qquad (5)$$

per g-atom of vanadium and $2J$ is the exchange integral, set equal to the singlet–triplet splitting. Calculated best-fit values of χ_M, J, g, and $N\alpha$ for both models are given in the Table. An example of the agreement between calculated and experimental susceptibilities is shown in the Figure. For the complex [VO(L)] [L = (III)] the average deviation, σ, in χ_M^{corr} is $16{\cdot}14 \times 10^{-6}$ for comparison with the infinite linear-chain model and $18{\cdot}66 \times 10^{-6}$ c.g.s. units for comparison with the dimetallic model. Therefore it is obvious that although a better fit is obtained by use of the linear-chain model, the difference is not great enough to allow one to assign a structure with certainty.

Magnetic data

[VO(L)],nX L = (I), X = EtCH, n = 1	$g = 1{\cdot}99$, $\theta = -7$ K, $N\alpha = 50 \times 10^{-6}$ c.g.s. units												
T/K	293	277	259	244	228	212	196	178	160	146	132	119	75
$10^6\chi_M^{corr}$ (obs.)/cm^3 g-atom^{-1}	1 295	1 376	1 499	1 540	1 622	1 744	1 928	2 030	2 173	2 480	2 746	2 970	4 844
μ_{eff}/B.M.	1·71	1·71	1·73	1·71	1·70	1·70	1·72	1·68	1·65	1·69	1·69	1·67	1·70
L = (II), X = H_2O, n = 1	$g = 1{\cdot}95$, $\theta = 0$ K, $N\alpha = 60 \times 10^{-6}$ c.g.s. units												
T/K	295	279	262	245	227	214	195	175	162	143	130	105	75
$10^6\chi_M^{corr}$ (obs.)/cm^3 g-atom^{-1}	1 270	1 360	1 409	1 517	1 658	1 745	1 891	2 075	2 291	2 527	2 832	3 450	4 820
μ_{eff}/B.M.	1·70	1·71	1·69	1·70	1·71	1·71	1·70	1·69	1·71	1·69	1·70	1·69	1·70
L = (III), n = 0	(A): * $g = 1{\cdot}82$; $J = -49$ cm^{-1}; $N\alpha = 80 \times 10^{-6}$ c.g.s. units (B): * $g = 1{\cdot}93$; $J = -58$ cm^{-1}; $N\alpha = 20 \times 10^{-6}$ c.g.s. units												
T/K	298	276	255	240	219	199	179	164	150	120	110	87	
$10^6\chi_M^{corr}$ (obs.)/cm^3 g-atom^{-1}	977	1 023	1 105	1 163	1 249	1 340	1 416	1 491	1 597	1 703	1 763	1 869	
[(A), calc.]	985	1 044	1 110	1 159	1 237	1 321	1 415	1 492	1 569	1 739	1 790	1 852	
[(B), calc.]	986	1 046	1 107	1 159	1 238	1 321	1 413	1 488	1 562	1 725	1 776	1 861	
μ_{eff}/B.M.	1·48	1·46	1·51	1·50	1·44	1·43	1·40	1·38	1·36	1·26	1·22	1·13	
L = (IV), n = 0	(A): * $g = 1{\cdot}80$; $J = -54$ cm^{-1}; $N\alpha = 100 \times 10^{-6}$ c.g.s. units (B): * $g = 1{\cdot}85$; $J = -63$ cm^{-1}; $N\alpha = 120 \times 10^{-6}$ cg.s. units												
T/K	294	283	275	241	221	199	175	155	142	122	86		
$10^6\chi_M^{corr}$ (obs.)/cm^3 g-atom^{-1}	990	1 019	1 066	1 161	1 217	1 255	1 350	1 445	1 521	1 596	1 691		
[(A), calc.]	980	1 008	1 029	1 128	1 196	1 279	1 380	1 471	1 531	1 618	1 659		
[(B), calc.]	1 002	1 028	1 048	1 114	1 205	1 282	1 375	1 459	1 515	1 598	1 687		
μ_{eff}/B.M.	1·49	1·48	1·49	1·46	1·44	1·39	1·35	1·32	1·29	1·23	1·06		
L = (V), n = 0	(A): * $g = 1{\cdot}80$; $J = -58$ cm^{-1}; $N\alpha = 100 \times 10^{-6}$ c.g.s. units (B): * $g = 1{\cdot}85$; $J = -68$ cm^{-1}; $N\alpha = 120 \times 10^{-6}$ c.g.s. units												
T/K	295	276	242	222	206	184	160	144	134	89			
$10^6\chi_M^{corr}$ (obs.)/cm^3 g-atom^{-1}	956	1 026	1 130	1 200	1 254	1 304	1 373	1 408	1 442	1 581			
[(A), calc.]	965	1 011	1 105	1 169	1 224	1 305	1 400	1 463	1 500	1 532			
[(B), calc]	982	1 025	1 113	1 171	1 221	1 295	1 381	1 439	1 473	1 558			
μ_{eff}/B.M.	1·46	1·47	1·44	1·43	1·40	1·36	1·30	1·25	1·22	1·05			
L = (VI), n = 0													
T/K	298	275	244	226	206	185	162	141	124	89			
$10^6\chi_M^{corr}$ (obs./cm^3 g-atom^{-1}	1 468	1 559	1 741	1 817	1 817	1 908	1 969	2 075	2 151	2 151			
μ_{eff}/B.M.	1·84	1·82	1·82	1·79	1·71	1·66	1·58	1·51	1·45	1·23			

* (A), Parameters for dimetallic model; (B), parameters for infinite linear chain.

Ginsberg has investigated the magnetic properties of some copper(II)[15] and oxovanadium(IV)[5] complexes with tridentate Schiff's bases and suggested dimetallic structures to account for the antiferromagnetic behaviour. Only one i.r. VO stretching absorption was observed for our complexes, as expected for the dimetallic structure proposed by Ginsberg. The VO absorption wavenumbers were 989, 992, and 990 cm^{-1} for the complexes with L = (I), (II), and (III), respectively. These absorptions are quite typical for oxovanadium(IV) com-

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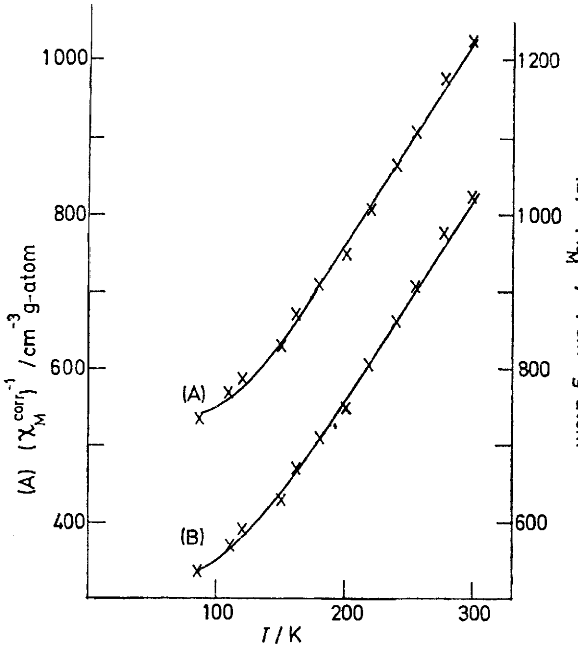
plexes. Recently the crystal structure of the complex [*NN'*-propylenebis(salicylaldiminato)]oxovanadium(IV) has been reported.[16] The crystal consists of infinite linear chains of molecules linked by$\cdots$V–O–V$\cdots$ bonds. The VO stretching wavenumber for this complex is only 854 cm^{-1}, the lowest ν(V=O) wavenumber reported to date. Goodgame and Waggett[17] have made a cryomagnetic study of this complex and report that no significant spin coupling between metal ions occurs. Therefore the ' normal ' VO stretching frequencies of our complexes do not support a linear-chain structure in which the vanadyl oxygen atom is utilized, and we are inclined to favour the dimetallic structure even though the linear chain is a slightly better fit to the magnetic data. The insolubility of the complexes in proper solvents precluded molecular-weight measurements.



Magnetic susceptibilities of the complex [VO(L)] [L = (III): (X), experimental; (A), Calculated for $J = -49$ cm^{-1}, $g = 1{\cdot}82$, and $N\alpha = 80 \times 10^{-6}$ c.g.s. units (dimetallic model); and (B), calculated for $J = -58$ cm^{-1}, $g = 1{\cdot}93$, and $N\alpha = 20 \times 10^{-6}$ c.g.s. units (linear-chain model)

It has been shown[15,18] that exocyclic chelate-ring substituents have a pronounced effect on the exchange energy, $2J$, for some dimetallic copper(II) complexes, but our results with oxovanadium(IV) ion show, as did those of Ginsberg *et al.*[5] that the exchange energy is insensitive to ring substituents. This difference in behaviour is probably due to a difference in exchange mechanism. It has been suggested that a direct σ-overlap is involved in the V–V interaction, but that superexchange *via* bridging oxygen atoms determines the Cu–Cu interaction in analogous complexes.[5,15] The general co-ordination about the vanadium atom in these complexes is assumed to be a distorted square pyramid. For square-pyramidal oxovanadium(IV) complexes the unpaired electron is in the $3d_{xy}$ orbital.[19] In dimetallic structures, as proposed by Ginsberg, the $3d_{xy}$ orbitals have the correct geometry to σ-bond to each other, and this direct V–V interaction should be the principal path for spin-spin coupling to occur. Thus the exchange energy should be somewhat insensitive to the ring substituents and primarily dependent on the degree of overlap between the $3d_{xy}$ orbitals.

Several unsuccessful attempts were made to fit the magnetic data of the complex [VO(L)] [L = (VI)] to antiferromagnetic-susceptibility theories. The magnetic moment decreases significantly as the temperature is decreased, and a plot of $1/\chi_M^{corr}$ against T yielded a straight line with a rather large Weiss constant of −250 K. Components to represent the ' odd or even effect ' of spins in a chain, and to account for paramagnetic impurities, were included in the equations, but still no reasonable fit could be obtained. We can offer no explanation for this except to suggest that the structure is different or perhaps more than one of the possible isomeric forms[20] are present in this complex.

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