region tails to higher frequencies (Figure 3), suggesting the presence of two component bands with the same sign. The maximum of the observed circular dichroism band, which reflects the position of the major component, lies at a lower frequency (19,400 cm^{-1}) than that of the visible absorption band of $(Co(NH_3)_6)^{3+}$. Accordingly it is concluded that $(+)(Co(en)_2sar)^{2+}$, which gives a positive dichroism band in the visible region, has the same absolute configuration of the chelate rings around the metal ion as $(+)(Co(en)_3)^{3+}$; that is, the mirror-image of the configuration shown in Figure 4a. It follows from the RD curve analysis that the $(-)(Co(NH_3)_4sar)^{2+}$ ion has the configuration for coordinated sarcosine given in Figure 1.

The absolute configurations of both these ions are at present being determined also by an X-ray crystallographic analysis.

Acknowledgment.—The authors are indebted to Dr. J. Fildes for the C, H, and N microanalyses.

Contribution from the Bell Telephone Laboratories, Inc.,
Murray Hill, New Jersey 07971

Magnetic Exchange in Transition Metal Complexes. III. Vanadyl Complexes with Tridentate Schiff Bases[1]

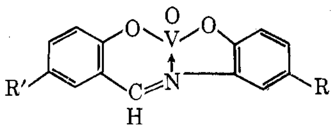
By A. P. GINSBERG, E. KOUBEK, and H. J. WILLIAMS

Received March 3, 1966

The magnetic susceptibility of a series of 5-substituted N-(2-hydroxyphenyl)salicylideneimine complexes of VO^{2+} (I) has been measured between 1.4 and 300°K. For R = H, R′ = H, CH_3, Cl, Br, NO_2 and R = Cl, R′ = H, Cl, the temperature dependence of the susceptibility is characteristic of magnetically isolated exchange coupled (antiferromagnetic) pairs. The complex is presumably dimeric, with a structure like that of the corresponding copper compounds. Infrared spectra were determined in the 800–1100-cm^{-1} region, and the VO stretching frequencies are assigned. In the R = H, R′ = NO_2 complex, there is evidence for a weak intermolecular interaction between vanadyl oxygen atoms and vanadium atoms. Exchange integrals are derived by fitting the susceptibilities to the theoretical equation for coupled pairs. The results are interpreted in terms of a direct σ metal–metal interaction between unpaired spins in the $3d_{xy}$ orbitals of the vanadium atoms. This is in contrast to the analogous copper complexes, where spin coupling takes place by superexchange through the bridging oxygen atoms.

Introduction

Several 5-substituted N-(2-hydroxyphenyl)salicylideneimine complexes of copper(II) have been shown to be magnetic dimers;[1] that is, the copper atoms are arranged in the crystal lattice as magnetically isolated exchange coupled pairs. The corresponding vanadyl complexes



I

with R = H, R′ = H, Cl, Br and R = NO_2, R′ = Br were reported[2,3] to have abnormally low magnetic moments (0.77–1.55 BM) at room temperature. It seems likely that these low moments result from antiferromagnetic exchange coupling between pairs of vanadyl ions, as suggested by Zelentsov.[3] In order to establish whether or not this is correct, we have determined the temperature dependence of the magnetic susceptibility of complex I with R = H, R′ = H, CH_3, Br, NO_2; R = Cl, R′ = H, Cl; and R = NO_2, R′ = H, NO_2,[4] between 1.4 and 300°K. With the exception of the R = NO_2, R′ = NO_2, H compounds, the results are in good agreement with the theoretical equation for exchange-coupled pairs. Presumably, the vanadyl complexes which show coupled-pair susceptibility have the same dimeric, oxygen-bridged structure as the copper complexes.[1,5]

Although pairwise magnetic exchange is well known in d^9 copper complexes[6] (unpaired spin in an orbital derived from the e_g set), our results represent the first demonstration of this phenomenon in a vanadyl complex (unpaired spin in an orbital derived from the t_{2g} set). The exchange integrals calculated from the susceptibility data show a quite different dependence on the substituents R and R′ than do the exchange integrals for the analogous copper complexes. The results are interpreted in terms of direct metal–metal interaction between pairs of vanadium atoms. This is in contrast to the copper complexes, where spin coupling takes place by superexchange *via* the bridging oxygen atoms.

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[1] Part II of this series: A. P. Ginsberg, R. C. Sherwood, and E. Koubek, *J. Inorg. Nucl. Chem.*, in press.

[2] V. V. Zelentsov, *Dokl. Akad. Nauk SSSR*, **139**, 1110 (1961).

[3] V. V. Zelentsov, *Russ J. Inorg. Chem.*, **7**, 670 (1962).

[4] The compounds with R = H, R′ = CH_3, NO_2; R = Cl, R′ = H, Cl; and R = NO_2, R′ = H, NO_2 do not appear to have been prepared previously.

[5] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

[6] See the references cited in ref 1.

TABLE I

ANALYSES OF VANADYL–SCHIFF BASE COMPLEXES

Complex I			Calcd %				Found %			
R	R′	Stoichiometry	C	H	N	V	C[a]	H[a]	N[a]	V
H	H	$C_{13}H_9NO_3V$	56.1	3.24	5.03	18.3	56.3	3.37	4.74	18.0
H	CH_3	$C_{14}H_{11}NO_3V$	57.6	3.79	4.79	17.4	57.7	3.71	4.86	17.5
H	Cl	$C_{13}H_8ClNO_3V$	49.9	2.56	4.48	16.3	50.0	2.73	4.59	16.4
H	Br	$C_{13}H_8BrNO_3V$	43.7	2.23	3.92	14.3	43.6	2.20	3.78	14.4
H	NO_2	$C_{13}H_8N_2O_5V$	48.3	2.50	8.67	15.8	48.3	2.80	8.76	16.1
Cl	H	$C_{13}H_8ClNO_3V$	49.9	2.56	4.48	16.3	50.2	2.58	4.65	16.0
NO_2	H	$C_{13}H_8N_2O_5V$	48.3	2.50	8.67	15.8	49.3	3.26	7.91	15.2
Cl	Cl	$C_{13}H_7Cl_2NO_3V$	45.0	2.16	4.04	14.7	45.0	2.14	4.13	14.9
NO_2	NO_2	$C_{13}H_7N_3O_7V$[b]	42.4	2.17	11.4	13.8	42.3	2.96	10.4	13.1
H	Cl monopyridinate	$C_{18}H_{13}ClN_2O_3V$	55.3	3.35	7.16	10.8	55.5	3.52	6.88	...

[a] By Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [b] Calcd for $C_{13}H_7N_3O_7V \cdot 0.5H_2O \cdot C_2H_5OH$: C, 42.0; H, 2.77; N, 10.5; V, 12.7.

Experimental Section

The ligands were prepared as described previously.[1] The complexes were formed by allowing a saturated aqueous solution of $VOCl_2$ (K & K Laboratories, shown by emission spectrographic analysis to be free of transition metal impurities) to react with about 10% less than the stoichiometric amount of ligand in ethanol. The mixture was refluxed for 3 hr, and then the brown, granular precipitate that had formed was filtered off, washed with hot ethanol, and dried at 0.1 mm, 80°. A sample of the unsubstituted complex (R = R′ = H) was also prepared under anhydrous conditions by refluxing anhydrous $VOCl_2$[7] with the ligand in absolute ethanol. A pyridine adduct of the R = H, R′ = Cl complex was prepared by dissolving the complex in excess pyridine and precipitating with water. The product was dried over P_2O_5 in an evacuated desiccator. Analytical results are summarized in Table I. Vanadium was determined by a standard procedure[8] after decomposing the compound with a mixture of concentrated sulfuric acid and fuming nitric acid. The R = H, R′ = Cl, Br compounds were analyzed for active hydrogen (Schwarzkopf Microanalytical Laboratory) by treating a benzyl ether solution of the complex with lithium aluminum hydride and measuring the H_2 evolved. In both cases no active hydrogen was found.

Infrared spectra of the complexes in pressed KBr disks and fluorocarbon oil mulls were measured with a Perkin-Elmer Model 337 grating spectrophotometer. Magnetic susceptibilities were measured between 1.4 and 300°K on a null-coil pendulum magnetometer[9] as described previously.[1] All measurements were made at a field strength of 14,240 oersteds.

Results

Composition of the Complexes.—Zelentsov[3] concluded, from analyses for vanadium and nitrogen, that the R = H, R′ = H, Cl, Br complexes form as monohydrates. However, our analytical results (Table I) for these compounds, as well as for the R = H, R′ = CH_3, NO_2 and R = Cl, R′ = H, Cl compounds, are in good agreement with the anhydrous complex I formulation. The absence of water or alcohol was confirmed by the absence of absorption in the OH stretching region of the infrared spectra. For the R = H, R′ = Cl, Br compounds, still further confirmation of the absence of hydroxylic solvent was provided by the negative results of analyses for active hydrogen. Finally, the R = H, R′ = Cl compound was prepared under anhydrous conditions, and the product was identical with that obtained in the presence of water. The method of preparation differs from that of Zelentsov only in the use of ethanol instead of methanol as solvent and in refluxing the mixture before filtering off the product.

Agreement between the analytical results for the R = NO_2, R′ = H, NO_2 compounds and the calculated values for anhydrous complex I is not so good as for the other compounds. The infrared spectrum of the R = NO_2, R′ = NO_2 compound has a band at ~3300 cm^{-1} which may be attributed to ν(OH) of water or alcohol in the molecule. To account for the analytical results, it is necessary to assume that *both* ethanol and water are present (*cf.* Table I). In the case of the R = NO_2, R′ = H compound, the infrared spectrum does *not* show absorption in the ν(OH) region; the presence of water or alcohol is therefore excluded. We consider this substance to have the anhydrous complex I formula.

The R = H, R′ = Cl complex reacts with pyridine to form a monopyridinate. The copper complex with N-(2-hydroxyphenyl)salicylideneimine behaves in the same way.[10]

VO Stretching Frequencies.—By comparing the infrared spectra of the vanadyl complexes with the spectra of the corresponding copper complexes, and of the free ligand, in the 800–1100-cm^{-1} region,[11] it was possible to identify the VO stretching frequencies. The assignments are given in Table II. In the case of the R = NO_2, R′ = H complex, the assignment of ν(VO) is ambiguous. Figure 1 shows the infrared spectrum of this compound between 880 and 1070 cm^{-1}; also shown are the spectra of the copper complex and of the free ligand. The bands at 891 and 911 cm^{-1} may be attributed to the ligand in the complex. ν(VO) must be one or more of the bands at 971, 985, 1030, and 1045 cm^{-1}. All of the other complexes, including the monopyridinate with R = H, R′ = Cl, have a VO stretching frequency in the range 990 ±

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(7) Prepared as described in "Handbuch der Preparativen Anorganischen Chemie," Vol. 2, G. Brauer, Ed., 2nd ed, Ferdinand Enke, Stuttgart, 1962, p 1105.

(8) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," revised ed, The Macmillan Co., New York, N. Y., 1943, p 724.

(9) R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

(10) M. Kishita, Y. Muto, and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957).

(11) In most vanadyl complexes, the V=O stretching band occurs between 1035 and 935 cm^{-1}: J. Selbin, L. H. Holmes, and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963)

Table II

VO Stretching Frequencies in Vanadyl–Schiff Base Complexes[a]

Complex I		
R	R′	ν(VO), cm^{-1}
H	H	990 s
H	CH_3	993 s
H	Cl	992 s
H	Br	991 s
H	NO_2	1010 m, 900 vs
Cl	H	1000 s, 989 s
NO_2	H	*b*
Cl	Cl	983 s, 993 s
NO_2	NO_2	999 s
H	Cl monopyridinate	978 s

[a] Measured on samples in pressed KBr disks: s, strong; m, medium; v, very. [b] See Discussion in text.

20 cm^{-1}. The R = H, R′ = NO_2 complex is unique in having a very strong absorption at 900 cm^{-1}. We assign this also as ν(VO) because the copper complex and the free ligand absorb only weakly around 900 cm^{-1}.

Magnetic Susceptibilities.—The magnetic susceptibility measurements are summarized in Table III. The susceptibility values χ_A' are per gram-atom of vanadium and include a diamagnetic correction. The R = NO_2, R′ = NO_2 complex and the monopyridinate of the R = H, R′ = Cl complex are Curie–Weiss paramagnets over the entire temperature range studied. A least-squares fit to the Curie–Weiss law

$$\frac{1}{\chi_A'} = \frac{1}{C}T + \frac{\theta}{C}$$

gave the following values for the Weiss constant θ and the effective magnetic moment $\mu'_{\mathrm{eff}} = 2.839(C)^{1/2}$: for the dinitro derivative, $\theta = 1.41 \pm 2°$ and $\mu'_{\mathrm{eff}} = 1.62 \pm 0.01$ BM; for the monopyridinate, $\theta = 2.06 \pm 5°$ and $\mu'_{\mathrm{eff}} = 1.75 \pm 0.03$ BM. The uncertainties are 99% confidence limits. The R = NO_2, R′ = H complex shows only a weak temperature-independent paramagnetism. All of the other compounds in Table III have χ_A' increasing to a maximum and then decreasing with decreasing temperature until, at quite low temperatures ($\sim$20°K), χ_A' passes through a minimum and then increases with decreasing temperature. Figure 2 illustrates this behavior with a plot of χ_A' *vs.* T for the R = H, R′ = Br complex.

The low-temperature rise in susceptibility of the vanadyl complexes, for which χ_A' passes through a maximum at higher temperatures, is very similar to the behavior of the dimeric copper complexes with the same ligands.[1] As before,[1] we attribute this effect to the presence of small amounts of a paramagnetic impurity, probably a solvated monomer of complex I. The vanadyl complex which forms with the R = NO_2, R′ = NO_2 ligand is an example of such a compound. If it is assumed that the susceptibility at 1.4°K is due entirely to an impurity with $\mu_{\mathrm{eff}} = 1.73$ BM, then the percentage of impurity required to give the observed susceptibility is as shown in Table IV. Such relatively small amounts of the type of impurity postulated would not affect the analytical results.

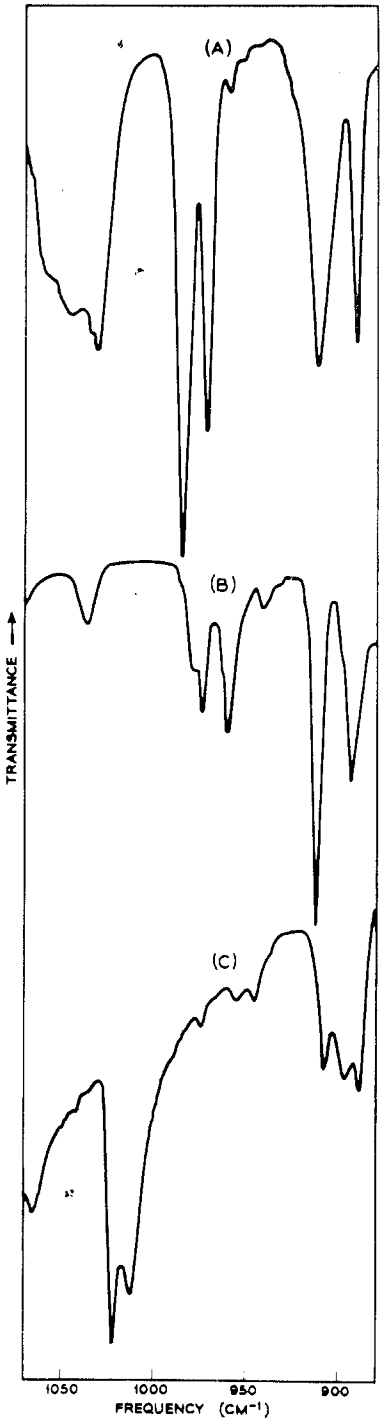

Figure 1.—Infrared spectra from 880 to 1070 cm^{-1} of: (A) complex I (R = NO_2, R′ = H); (B) the corresponding Cu complex; (C) the free ligand.

In order to correct the measured susceptibilities for the impurity contribution and to determine $N\alpha$, the temperature-independent paramagnetism, the same procedure described earlier was used.[1] The $N\alpha$ values and the corrected susceptibilities, χ_A'(cor), are given in Table III. Figure 2 shows a plot of χ_A'(cor) for the R = H, R′ = Br complex. The underlined values of χ_A' in Table III are the basis for the determination of $N\alpha$ and the impurity correction. Also listed in

TABLE III

MAGNETIC SUSCEPTIBILITIES[a] (CGS/G-ATOM OF VANADIUM) AND EFFECTIVE MOMENTS (BM)[b,c]

Complex (I) R = H, R′ = H; $N\alpha = 20 \times 10^{-6}$

T, °K	1.4	4.2	15	20	23	25	28	33	36	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120	125
$10^4\chi_A'$	63.4	27.1	8.57	6.66	5.93	6.10	5.88	6.53	6.80	8.61	9.68	10.7	11.6	12.5	13.3	13.9	14.4	14.7	15.1	15.3	15.4	15.4	15.5	15.5	15.5	15.3
$10^4\chi_A'$(corr.)	0.19	0.20	0.20	0.31	0.39	0.99	1.30	2.64	3.23	5.74	7.09	8.32	9.43	10.5	11.5	12.2	12.8	13.2	13.6	14.0	14.1	14.1	14.3	14.3	14.4	14.2
μ_{eff}	--	--	--	--	--	0.13	0.16	0.25	0.30	0.45	0.53	0.60	0.67	0.74	0.80	0.85	0.90	0.94	0.99	1.03	1.06	1.08	1.12	1.14	1.17	1.19

T, °K	130	138	148	160	165	179	195	210	225	240	255	273	285	299
$10^4\chi_A'$	15.2	14.9	14.7	14.3	14.1	13.4	13.0	12.4	12.0	11.6	11.0	10.3	10.1	9.78
$10^4\chi_A'$(corr.)	14.2	14.0	13.8	13.5	13.3	12.7	12.4	11.8	11.4	11.1	10.5	9.84	9.63	9.34
μ_{eff}	1.21	1.24	1.27	1.31	1.32	1.34	1.38	1.40	1.42	1.45	1.46	1.46	1.47	1.48

Complex (I) R = H, R′ = CH_3; $N\alpha = 70 \times 10^{-6}$

T, °K	1.4	4.2	10.5	23.2	34.8	46	61.5	77	94	107	113	138	153	154	164	171.5	201	224	239	269.5	294
$10^4\chi_A'$	14.0	6.87	3.48	2.27	4.14	7.45	12.0	15.3	16.6	16.6	16.4	15.5	14.8	15.1	14.2	14.2	12.8	12.0	11.4	10.5	9.77
$10^4\chi_A'$(corr.)	0.65	0.71	0.70	0.95	3.25	6.77	11.5	14.9	16.3	16.3	16.1	15.2	14.6	14.9	14.0	14.0	12.6	11.9	11.3	10.4	9.66
μ_{eff}	--	--	--	--	0.27	0.47	0.73	0.94	1.09	1.16	1.18	1.27	1.31	1.32	1.33	1.36	1.39	1.42	1.43	1.45	1.46

Complex (I) R = H, R′ = Cl; $N\alpha = 100 \times 10^{-6}$

T, °K	1.4	4.2	8.6	11.7	13.7	15.4	18.1	21	25	30	35	40	45	50	55	60	65	70	75	80	85	91	95	100	105	110
$10^4\chi_A'$	18.7	9.04	5.33	5.15	4.31	3.72	3.83	5.95	5.60	8.38	10.9	13.8	15.9	17.9	19.3	20.6	21.6	22.1	21.8	22.1	21.7	21.5	21.4	21.5	21.2	21.0
$10^4\chi_A'$(corr.)	0.99	1.00	1.00	1.88	1.49	1.19	1.67	4.07	4.01	7.05	9.75	12.8	15.0	17.1	18.6	19.9	20.9	21.6	21.3	21.6	21.2	21.1	20.9	21.1	20.8	20.6
μ_{eff}	--	--	--	--	--	--	--	0.23	0.25	0.38	0.50	0.62	0.71	0.81	0.88	0.96	1.02	1.08	1.11	1.15	1.18	1.21	1.24	1.27	1.29	1.32

T, °K	117	124	130	146	174	192	218	256	296
$10^4\chi_A'$	20.5	20.0	19.1	18.3	16.7	16.1	14.3	12.5	11.0
$10^4\chi_A'$(corr.)	20.2	19.7	18.8	18.1	16.4	15.9	14.2	12.4	10.9
μ_{eff}	1.34	1.37	1.37	1.42	1.47	1.52	1.52	1.53	1.54

Complex (I) R = H, R′ = Br; $N\alpha = 30 \times 10^{-6}$

T, °K	4.2	6.0	15	21	26	32	38	45	50	56	62	69	76	83	89	96	102	109	116	122	130	140	150	160	170	185
$10^4\chi_A'$	4.54	2.92	1.20	1.46	2.25	3.69	5.29	7.82	9.39	10.8	12.3	14.0	15.1	15.9	16.2	16.5	16.8	16.7	16.6	16.4	16.2	15.7	15.1	14.8	14.3	13.6
$10^4\chi_A'$(corr.)	0.30	0.30	0.30	0.84	1.75	3.29	4.95	7.54	9.14	10.6	12.1	13.8	14.9	15.8	16.1	16.4	16.6	16.6	16.5	16.4	16.1	15.6	15.0	14.7	14.2	13.6
μ_{eff}	--	--	--	--	0.17	0.28	0.38	0.51	0.60	0.68	0.77	0.87	0.95	1.02	1.06	1.11	1.16	1.20	1.23	1.26	1.29	1.31	1.33	1.36	1.38	1.41

T, °K	200	215	236	250	270	285	299
$10^4\chi_A'$	13.1	12.7	11.9	11.4	10.7	10.3	9.72
$10^4\chi_A'$(corr.)	13.1	12.6	11.9	11.3	10.7	10.3	9.67
μ_{eff}	1.44	1.46	1.48	1.49	1.50	1.51	1.50

Complex (I) R = H; R′ = NO_2; $N\alpha = 100 \times 10^{-6}$

T, °K	1.4	4.2	9.0	16	20	24	28	32	36	40	45	50	55	60	70	77	79	81	86	88	101	108	116	132	137	147
$10^4\chi_A'$	32.6	12.4	6.45	3.98	3.30	2.92	2.69	3.58	2.54	2.14	2.40	2.56	3.04	3.30	3.72	3.97	4.90	4.94	4.89	4.99	6.25	6.70	7.23	8.25	8.42	8.74
$10^4\chi_A'$(corr.)	1.08	0.98	1.00	0.88	0.82	0.85	0.91	2.02	1.16	0.89	1.29	1.56	2.13	2.47	3.01	3.32	4.26	4.32	4.31	4.42	5.76	6.24	6.80	7.87	8.06	8.40
μ_{eff}	--	--	--	--	--	--	--	--	--	--	0.10	0.15	0.22	0.27	0.34	0.38	0.46	0.47	0.48	0.49	0.62	0.68	0.74	0.86	0.88	0.94

T, °K	150	162	168	178	188	195	205	225	236	245	254	264	271	278	285	292	298
$10^4\chi_A'$	9.05	9.19	9.45	9.27	9.39	9.43	9.41	9.29	9.31	9.11	8.94	8.80	8.59	8.49	8.28	8.23	8.18
$10^4\chi_A'$(corr.)	8.72	8.88	9.15	8.99	9.12	9.17	9.17	9.07	9.10	8.91	8.74	8.61	8.40	8.31	8.10	8.06	8.01
μ_{eff}	0.97	1.01	1.05	1.07	1.11	1.13	1.16	1.21	1.24	1.25	1.26	1.27	1.27	1.28	1.28	1.29	1.30

Complex (I) R = Cl, R′ = H; $N\alpha = 50 \times 10^{-6}$

T, °K	1.4	4.2	14	22.3	34.8	46.5	59.5	82	91	105	111.5	123.5	140.5	183.5	208	226	238.5	261	294
$10^4\chi_A'$	22.8	9.46	3.40	2.71	4.68	7.66	11.3	15.3	16.1	16.2	16.1	15.8	15.2	13.5	12.4	11.7	11.2	10.7	9.73
$10^4\chi_A'$(corr.)	0.51	0.50	0.50	0.87	3.49	6.76	10.6	14.8	15.6	15.8	15.7	15.5	15.0	13.3	12.2	11.5	11.0	10.5	9.59
μ_{eff}	--	--	--	--	0.29	0.48	0.69	0.97	1.05	1.14	1.17	1.22	1.28	1.38	1.40	1.41	1.42	1.45	1.47

Complex (I) R = NO_2, R′ = H

T, °K	175	215	245	295
$10^4\chi_A'$	0.76	1.2	1.0	0.56

Complex (I) R = Cl, R′ = Cl; $N\alpha = \sim 25 \times 10^{-6}$

T, °K	1.435	4.2	10.0	14.6	21.3	30.9	34.9	42	45.7	61	62	72	81.5	90	101	111	115	120	123.5	124	124.5	149	150	170	185
$10^4\chi_A'$	10.4	2.98	1.20	0.93	0.68	1.85	2.47	4.49	5.09	9.47	9.52	11.6	13.0	13.9	14.5	14.9	14.7	14.9	14.9	14.9	15.0	14.7	14.8	13.8	13.3
$10^4\chi_A'$(corr.)	-0.08	0.42	0.21	0.26	0.23	1.54	2.20	4.27	4.89	9.32	9.37	11.5	12.9	13.8	14.4	14.8	14.6	14.8	14.8	14.8	14.9	14.6	14.7	13.8	13.2
μ_{eff}	--	--	--	--	--	0.18	0.23	0.37	0.41	0.67	0.67	0.81	0.91	0.99	1.08	1.14	1.16	1.19	1.20	1.21	1.21	1.31	1.32	1.36	1.39

T, °K	186	215	217	251	254	275	276	297
$10^4\chi_A'$	13.2	12.1	12.2	11.1	11.1	10.4	10.4	9.92
$10^4\chi_A'$(corr.)	13.2	12.1	12.1	11.0	11.0	10.4	10.4	9.89
μ_{eff}	1.39	1.43	1.44	1.48	1.48	1.50	1.50	1.52

Complex (I) R = NO_2, R′ = NO_2; $\mu_{eff}' = 1.62$

T, °K	1.46	4.2	7.05	8.3	14.2	15.1	20	27	33.4	41	50	51	62.5	63.5	72	83	94	106	115	139.5	140.5	141	162
$10^4\chi_A'$	1813	721	478	406	228	215	159	116	91.8	73.8	59.7	60.5	50.3	50.4	45.5	39.6	35.2	31.2	27.8	22.9	22.8	22.7	19.9

T, °K	163	177	179	201	201.5	217	218	234	241.5	243	263	266	299
$10^4\chi_A'$	19.9	18.1	18.1	16.0	15.9	14.8	14.8	14.0	13.4	13.3	12.3	12.2	11.3

Monopyridinate of Complex (I) R = H, R′ = Cl; $\mu_{eff}' = 1.75$

T, °K	1.4	4.2	8.0	21	35	55	71	90	105	120	151	161	185	203	215	234	254	271	297
$10^4\chi_A'$	1435	807	517	373	97.0	59.9	48.3	39.3	36.0	30.1	24.2	23.1	20.0	18.4	17.6	16.3	15.0	14.1	12.6

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[a] Corrected for the diamagnetism of all of the atoms in the molecule using corrections from P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956, pp 78, 92. [b] The $N\alpha$ values given in this table were obtained as described earlier;[1] they may be in error by as much as $\pm 50 \times 10^{-6}$. [c] Temperatures are accurate to at least ±0.1° below 50°K and to ±0.5° at higher temperatures.

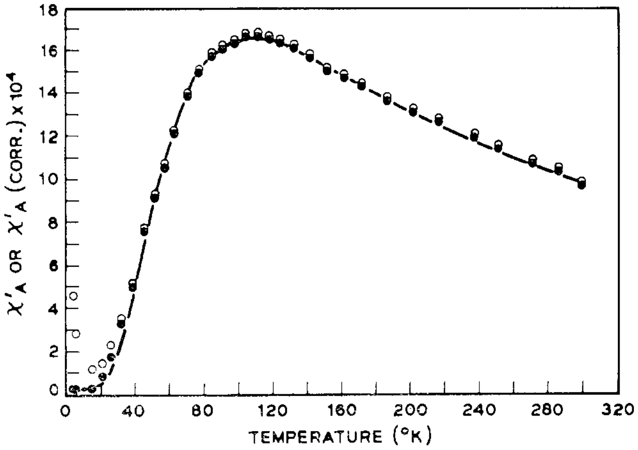


Figure 2.—Temperature dependence of the magnetic susceptibility of complex I (R = H, R' = Br): O, χ_A'; ●, χ_A'(cor). The solid line is a least-squares fit to the equation for coupled pairs, g = 1.89, J = 115 cm^{-1}, $N\alpha$ = 30 × 10^{-6}.

Table IV

Percentage of Paramagnetic Vanadyl Impurity Required to Give Observed χ_A' at 1.4°K[a]

Complex I		
R	R'	% paramagnetic impurity
H	H	2
H	CH_3	0.5
H	Cl	0.7
H	Br	0.5[b]
H	NO_2	1
Cl	H	0.8
Cl	Cl	0.4

[a] Based on the assumption that the impurity μ_{eff} = 1.73 BM and that the entire susceptibility at 1.4°K is due to the impurity. [b] This sample was not measured at 1.4°K; the estimation of the paramagnetic impurity was made from the 4.2°K point.

Table III are the effective magnetic moments at each temperature, calculated from the relation

$$\mu_{eff} = 2.839[(\chi_A'(\text{cor}) - N\alpha)T]^{1/2}$$

Discussion

Application of the least-squares-fitting program described earlier[1] showed that, for the compounds listed in Table V, the χ_A'(cor) *vs.* T curves can all be described by the susceptibility equation[12] for exchange-coupled pairs

$$\chi_A'(\text{cor}) = \frac{g^2N\beta^2}{3kT}[1 + {}^1/_3 \exp(J/kT)]^{-1} + N\alpha$$

where J is the exchange integral, set equal to the singlet–triplet splitting, and g is the magnetic field splitting factor. The variance of each fit and the values of g and J are given in Table V; also listed is the temperature at the maximum, obtained from the relation $T_{max} \simeq 5J/8k$. The calculated curve for the R = H, R' = Br complex is shown in Figure 2.

Table V

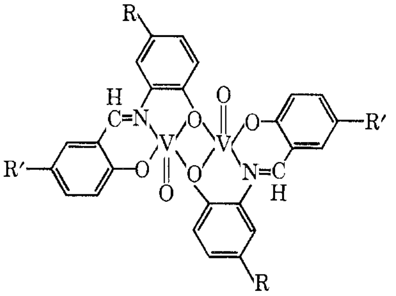
Vanadyl Complex I Compounds Which Follow the Susceptibility Equation for Exchange-Coupled Pairs

Compound		Variance of best fit × 10^{10}	g	J, cm^{-1}	T_{max}, °K
R	R'				
H	H	8.7	1.85 ± 0.1	125 ± 2	112
H	CH_3	5.3	1.86 ± 0.1	118 ± 2	106
H	Cl	20	1.89 ± 0.1	90 ± 2	81
H	Br	6.3	1.89 ± 0.1	115 ± 2	104
H	NO_2	6.0	1.83 ± 0.1	218 ± 5	196
Cl	H	3.1	1.86 ± 0.1	120 ± 2	108
Cl	Cl	3.5	1.92 ± 0.1	132 ± 2	119

The uncertainties given in Table V for g and J are estimates meant to reflect probable precision (as indicated by a duplicate determination on the R = H, R' = NO_2 compound) and also the effect of varying $N\alpha$ between 10 and 150 × 10^{-6}. The results in Table V establish the following order for the exchange integrals J(R,R')

$$J(\text{H,NO}_2) > J(\text{Cl,Cl}) \sim J(\text{H,H}) \sim J(\text{Cl,H}) \sim J(\text{H,CH}_3) \sim J(\text{H,Br}) > J(\text{H,Cl})$$

The vanadyl complexes which obey the susceptibility equation for coupled pairs are probably composed of dimeric molecules with a structure analogous to that proposed for the corresponding copper complexes[1,5]

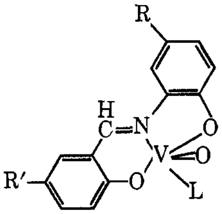


One infrared-active VO stretching frequency is expected for this structure, and this is what was observed (Table II) for the compounds with R = H, R' = H, CH_3, Cl, Br. However, for the compounds with R = H, R' = NO_2 and R = Cl, R' = H, Cl, two VO stretching frequencies were found. In the monochloro and dichloro derivatives the two bands are separated by only 10 cm^{-1}, so that the doubling of ν(VO) may be attributed to unit cell group splitting or to a crystal packing effect which causes the two vanadium atoms of the dimeric molecule to be nonequivalent.[13] In the R = H, R' = NO_2 complex the two bands are separated by 110 cm^{-1}. This is too large a separation to be caused by either unit cell group splitting or a crystal packing effect. Since one of the bands occurs at 900 cm^{-1}, much lower in energy than ν(VO) in any of the other Schiff base complexes, we suggest that in the R = H, R' = NO_2 complex, one of the vanadyl oxygen atoms in each dimer molecule interacts with a vanadium atom in a second molecule to form a tetramer or higher polymeric unit. Such a structure would have a susceptibility *vs.* temperature curve indistinguishable from the curve for isolated coupled pairs if the superexchange through the vanadyl oxygen atom is weak.

[12] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (London), **A214**, 451 (1952).

[13] A packing effect of this type has been observed in the related copper complex with N-(2-hydroxyphenyl)-2-acetyl-1-methylethylidenimine; see ref 5.

Of the compounds studied, three did not obey the dimer susceptibility equation. Two of these, the R = NO_2, R′ = NO_2 complex and the monopyridinate of the R = H, R′ = Cl complex, are Curie–Weiss paramagnets with small values of θ. We suggest that these two compounds are five-coordinated monomers in which a molecule of water, ethanol, or pyridine occupies one of the coordination positions



where R = NO_2, R′ = NO_2, L = H_2O or C_2H_5OH; R = H, R′ = Cl, L = C_5H_5N. An analogous structure has been proposed[14] for the paramagnetic monopyridinates of copper complexes with tridentate Schiff bases. Both of the paramagnetic vanadyl complexes have a single VO stretching frequency in the normal range for $\nu(V{=}O)$. μ'_{eff} for the monopyridinate is very close to the spin-only value and falls in the range (1.68–1.78 BM) usually observed for paramagnetic vanadyl complexes. μ'_{eff} for the dinitro complex is, for no evident reason, somewhat lower than expected.

The R = NO_2, R′ = H complex is the remaining compound which does not follow the singlet–triplet susceptibility curve; it has only a small temperature-independent paramagnetism. One possible interpretation of this result is that the compound has the same dimeric structure as the other complexes but that the exchange interaction is so strong that the spins are completely coupled at room temperature. However, in view of the rather small effects which the substituents have on the exchange interaction in the dimers, it seems more likely that the complete spin pairing in the R = NO_2, R′ = H complex means that this compound has a different structure. The infrared spectra give no evidence for bridging through the vanadyl oxygen atom.

The effect of the substituents R and R′ on the exchange integrals for the vanadyl dimers is quite different from their effect in the corresponding copper dimers.[1] In particular, in the copper complexes, it was found that electron-withdrawing groups usually increase the exchange interaction if they are introduced at the R′ position, but decrease it if they are introduced at the R position. In the vanadyl complexes, however, the exchange integrals are relatively unaffected by the substituents, except for $J(H,NO_2)$ and $J(H,Cl)$ which are, respectively, considerably larger and somewhat smaller than the other exchange integrals. The difference in behavior of the copper and vanadyl complexes may be attributed to a difference in the way in which exchange coupling takes place.

In the copper complexes, spin coupling takes place by superexchange through the bridging oxygen atoms. The magnitude of the exchange integral depends on the overlap between the metal atom magnetic orbital ($3d_{x^2-y^2}$) and the orbitals of the bridging atoms.[1] In the vanadyl complexes the situation is quite different. The coordination about the metal atom is assumed to be a distorted square pyramid. For square-pyramidal vanadyl complexes, the unpaired spin is expected to be in the $3d_{xy}$ orbital.[11,15] This is especially true for the present complexes, because two of the base atoms of the square pyramid are bridging oxygen atoms which are also bound to carbon atoms of the ligand molecule. Both the p_x and p_y orbitals of these oxygen atoms are involved in strong σ bonding and therefore do not π-donate to the vanadium $3d_{xy}$ orbitals (p_x has π symmetry with respect to d_{xy} of one vanadium atom while p_y has π symmetry with respect to d_{xy} of the second vanadium atom of the dimer). The $3d_{xy}$ orbital is therefore lowered in energy with respect to the $3d_{xz}$ and $3d_{yz}$ orbitals. In the binuclear complexes the $3d_{xy}$ orbitals have appropriate symmetry to σ bond with each other, and this σ metal–metal interaction should be the principal path for spin coupling.

Disregarding, for the moment, $J(H,NO_2)$ and $J(H,Cl)$, we may now rationalize the relative independence of $J(R,R')$ on R and R′. We assume (as with the copper complexes) that the structure of the ligand fixes the metal–metal distance in the dimer independently of the nature of the substituents R and R′. Changing R and R′ does, however, alter the effective charge on the metal atom. In the copper complexes[1] this results in a change in J, because alteration of the effective charge changes the overlap between the copper atom magnetic orbital and the bridging oxygen atom orbitals, which is the critical factor in determining the strength of the exchange coupling. For the vanadyl complexes, however, the strength of the exchange coupling is primarily determined by the direct overlap between the $3d_{xy}$ orbitals on the two vanadium atoms. The relative independence of $J(R,R')$ on R and R′ may then be interpreted as meaning that the overlap between the $3d_{xy}$ orbitals is relatively independent of small changes in the effective charge on the vanadium atoms. This is reasonable since altering the effective charge produces two opposing effects on the overlap. For example, if the effective charge on the vanadium atoms is increased, by substituting an electron-withdrawing group at R or R′, the $3d_{xy}$ orbitals should contract, thus tending to decrease the overlap, but the polarizing effect of each atom on its partner will be enhanced, thus tending to increase the overlap. Apparently, for most of the substituents studied, these two effects roughly cancel each other.

$J(H,Cl)$ and $J(H,NO_2)$ are exceptions to the above interpretation. The fact that $J(H,NO_2)$ is considerably higher than the other exchange integrals may be explained in the following way. We have already seen that the infrared spectrum of the R = H, R′ = NO_2

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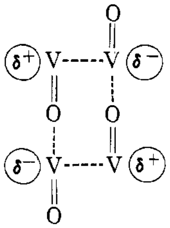
[14] M. Kubo, Y. Kuroda, M. Kishita, and Y. Muto, *Australian J. Chem.*, **16**, 7 (1963).

[15] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

complex indicates that one of the vanadyl oxygen atoms in each molecule is interacting with a vanadium atom in another molecule. A plausible arrangement is



As a consequence of this interaction, the effective charge of one vanadium atom in each pair increases while that of its partner decreases. The result should be an increase in the interaction between the paired vanadium atoms.

We can offer no explanation for the fact that J (H,Cl) is somewhat lower than the other exchange integrals, except to suggest that it may result from a crystal packing effect which somehow causes an increase in the V–V distance.

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Amides as Ligands. VI. Spectrochemical Studies of γ-Thiobutyrolactam and N-Methyl-γ-thiobutyrolactam Cobalt(II) Complexes[1]

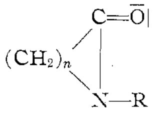
BY STANLEY K. MADAN AND MICHAEL SULICH[2]

Received March 21, 1966

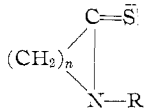
The syntheses, electronic absorption spectra, infrared spectra, magnetic susceptibilities, and conductance measurements of a series of cobalt(II) complexes of the general formulas $[Co(TBuL)_4](ClO_4)_2$, $[Co(NMTBuL)_4](ClO_4)_2$, $[Co(TBuL)_2X_2]$, and $[Co(NMTBuL)_2X_2]$ (TBuL = γ-thiobutyrolactam, NMTBuL = N-methyl-γ-thiobutyrolactam, and X = Cl, Br, I, SCN, and NO_3) are described. The usual ligand field parameters Dq, B', and β are calculated for these complexes. The parameters indicate that these complexes are tetrahedral and sulfur coordinated. The ligands TBuL and NMTBuL are each assigned a position relative to the other sulfur-containing donors in the spectrochemical series. With NMTBuL, an inductive effect, rather than a steric effect, previously observed for some fully substituted amides[3] and cyclic lactams,[4] is found to exist for the coordinated thiolactam. The $[Co(NMTBuL)_2(NO_3)_2]$ complex seems to possess an octahedral stereochemistry, a conclusion based on the electronic spectra, infrared spectra, and magnetic moment.

Introduction

The spectral and donor characteristics of a series of lactams with the general formula I (when n = 3, 4, 5 with R = H and CH_3) have been recently studied.[4,5]



I



II

The spectral parameters Dq and β have been measured for these lactams with nickel(II) perchlorate and chromium(III) perchlorate, in an octahedral field. However, the thiolactams[6,7] of the general formula II (when n = 3 with R = H and CH_3 or when n = 5 with R = H) produce tetrahedral coordination for the cobalt(II) ion.

Pursuant to our interest in substituted amides as ligands and sulfur as a donor atom, we have synthesized a series of cobalt(II) complexes with γ-thiobutyrolactam (TBuL) and N-methyl-γ-thiobutyrolactam (NMTBuL). We have measured the electronic parameters characterizing TBuL and NMTBuL as ligands and have assigned each a position relative to the other sulfur-containing donors in the spectrochemical series, in a tetrahedral field.[6,8–10] In addition, we have examined the effect on the Dq parameter of substituted and unsubstituted five-membered thiolactam coordinated to cobalt(II) perchlorate in a tetrahedral field.

Experimental Section

All materials used were reagent grade. The N-methyl-γ-butyrolactam was purchased from Aldrich Chemicals and was purified by vacuum distillation. The middle fraction collected at 80° (10 mm) (torr) was used for the preparation of NMTBuL. The γ-butyrolactam was used in the synthesis of TBuL without further purification. Fisher spectral grade nitromethane was employed for the spectral and conductance measurements. Anhydrous cobalt(II) iodide and cobalt(II) thiocyanate trihydrate were obtained from Alfa Inorganics.

Analytical Work.—Carbon, hydrogen, nitrogen, and sulfur analyses were performed by Weiler and Strauss, Microanalytical

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(1) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 14, 1966.

(2) Based in part on a dissertation to be submitted by M. Sulich to the Graduate School of the State University of New York at Binghamton in partial fulfillment of the requirements for the degree of Master of Arts, 1966.

(3) R. S. Drago, D. W. Meek, M. D. Joeston, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(4) J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Madan, *ibid.*, **4**, 18 (1965).

(5) S. K. Madan and H. H. Denk, *J. Inorg. Nucl. Chem.*, **27**, 1049 (1965).

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(7) This work.

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(10) S. K. Madan and D. Mueller, *J. Inorg. Nucl. Chem.*, **28**, 177 (1966).