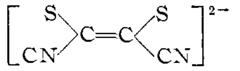
A SPIN-FREE SQUARE PLANAR COBALTOUS COMPLEX[1]

Sir:

The ligand maleonitriledithiolate (MNT) forms 2:1 complexes with a number of divalent metal ions, including Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{2+}, Zn^{2+} and Co^{2+}. The $R_2Ni(MNT)_2$, $R_2Pd(MNT)_2$ and $R_2Pt(MNT)_2$ [R = $(n\text{-}C_4H_9)_4N^+$] complexes have identical X-ray powder patterns, are diamagnetic in the solid and 1:2 electrolytes in acetone solution. Thus they must be square planar complexes. The electronic spectrum of $R_2Ni(MNT)_2$ in the solid or in solution (acetone, DMF) shows a near infrared band at 11,850 cm.$^{-1}$ (ϵ = 31.2). This band may be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ $(xy \rightarrow x^2-y^2)$ transition.[2] This is a very low energy band for diamagnetic square planar Ni^{2+} and indicates that the four sulfurs have an unusually weak ligand field strength in this particular complex.



The $R_2Co(MNT)_2$ complex is also a 1:2 electrolyte in acetone solution. The X-ray powder patterns for $R_2Co(MNT)_2$ and $R_2Pt(MNT)_2$ (also $R_2Ni(MNT)_2$) are identical, and differ considerably from the X-ray powder pattern obtained for $R_2Zn(MNT)_2$. Solid $R_2Co(MNT)$ has identical electro spin resonance (e.s.r.) spectra at 300° and 77°K. The $g_\perp$ value of 2.03 ± 0.01 clearly identifies the ground state as orbitally non-degenerate, and rules out an octahedral (g = 4.2785 for Co^{2+} in MgO[3]), tetragonal (g = 3.368 for $Co(py)_4Cl_2$[4]) or tetrahedral ($g_\parallel$ = 2.32, $g_\perp$ = 2.27 for Cs_3CoCl_5[5]; g = 2.3 for Co^{2+} in ZnS[6]) environment for the Co^{2+} in solid $R_2Co(MNT)_2$. The e.s.r. spectrum of a frozen acetone solution of $R_2Co(MNT)_2$ also gives $g_\perp$ = 2.03 ± 0.01.

TABLE I

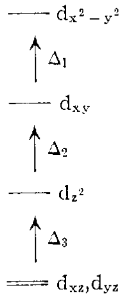
Complex			$R_2Ni(MNT)_2$	$R_2Co(MNT)_2$
Analytical	Carbon	Calcd.	58.37	58.27
		Found	58.11	58.14
	Hydrogen	Calcd.	8.81	8.79
		Found	8.81	8.28
	Nitrogen	Calcd.	10.21	10.17
		Found	10.19	9.91
X-Ray powder pattern			Identical with $R_2Pt(MNT)_2$	
Magnetic properties	μ_{eff}		Diamagnetic	3.92
	$g_\perp$(e.s.r.)		...	2.03 ± 0.01
Λ[a]			198	210

[a] Expressed in cm.^{2} mole^{-1} ohm^{-1} for 0.01 *M* acetone solutions at 26°.

The average magnetic moment of solid $R_2Co(MNT)_2$ is 3.92 B.M., corrected for diamagnetism and temperature independent paramagnetism. This moment is very nearly the spin-only value (3.88 B.M.) for three unpaired electrons, is in agreement with the e.s.r. result (very small orbital contribution) and is conspicuously different from typical moments for octahedrally (4.3–5.2 B.M.)[7] and tetrahedrally (4.2–5.0)[8] coördinated Co^{2+} complexes.

TABLE II

ORBITAL AND INTERELECTRONIC-REPULSION ENERGIES OF THE MOST STABLE STATES FOR d^7 AND d^8 SQUARE PLANAR COMPLEXES



	Configuration	Term	Orbital energy	Slater-Condon energy
d^7	$(xz)^2(yz)^2(z^2)^2(xy)$	$^2B_{2g}$	[a]	[a]
	$(xz)^2(yz)^2(z^2)(xy)(x^2-y^2)$	$^4A_{2g}$	$\Delta_1 + \Delta_2$	$-24F_2 - 20F_4$
	$(xz)^2(yz)^2(z^2)(xy)^2$	$^2A_{1g}$	Δ_2	$-20F_2 + 100F_4$
d^8	$(xz)^2(yz)^2(z^2)^2(xy)^2$	$^1A_{1g}$	[a]	[a]
	$(xz)^2(yz)^2(z^2)^2(xy)(x^2-y^2)$	$^3A_{2g}$	Δ_1	$-105F_4$
	$(xz)^2(yz)^2(z^2)(xy)^2(x^2-y^2)$	$^3B_{1g}$	$\Delta_1 + \Delta_2$	$-12F_2 - 45F_4$

[a] Taken as the reference point.

Table I summarizes the data given above concerning the $R_2Ni(MNT)_2$ and $R_2Co(MNT)_2$ complexes. The only reasonable conclusion that can be drawn from the combined analytical, conductance, X-ray, e.s.r. and static susceptibility data is that $R_2Co(MNT)_2$ is the first well-characterized, rigorously square planar and spin-free metal complex.[9,10]

The most interesting result is that the same ligand gives a spin-paired ground state for a square planar Ni^{2+} complex and a spin-free ground state for a square planar Co^{2+} complex. This situation is consistent with the theoretical prediction that the $^4A_{2g}$ state for square planar Co^{2+} is relatively more stable (compared with $^2B_{2g}$ and $^2A_{1g}$) than either the $^3A_{2g}$ or $^3B_{1g}$ states (compared to $^1A_{1g}$) for square planar Ni^{2+} (see Table II), assuming that the orbital parameters Δ_1, Δ_2 and Δ_3 do not change significantly in going from Ni^{2+} to Co^{2+}. The value of Δ_1 may be obtained from the first *d–d* band in $R_2Ni(MNT)$. Reasonable estimates $F_2 = 10F_4$ =

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[7] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," eds. J. Lewis and R. G. Wilkins, Interscience Publishers, Inc., New York, N. Y., 1960, p. 406.

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[9] F. A. Cotton and R. H. Holm (ref. 8) have presented magnetic susceptibility and optical spectral evidence for the existence of spin-free, planar Co^{2+} complexes containing four oxygen donor atoms. The magnetic moments of these complexes are in the range 4.74–5.04 B.M., indicating a considerable orbital contribution. To explain this orbital contribution Cotton and Holm assume the energy order $d_{xz}, d_{yz} > d_{z^2}$ (which gives a ^4E_g ground state), while the order for the orbital non-degeneracy observed for $R_2Co(MNT)_2$ must be $d_{z^2} > d_{xz}, d_{yz}$. It is possible (ref. 2) that both energy orders exist for square planar metal complexes, but more direct structural evidence is needed before the CoO_4 type complexes of ref. 8 can be considered square planar.

[10] There are no known examples of rigorously square planar, spin-free Ni^{2+}, although C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959), have indicated such a possibility, provided Δ_1 is less than 10,000 cm.$^{-1}$. For a recent discussion of magnetically anomalous Ni^{2+} complexes, see R. H. Holm. *ibid.*, **83**, 4683 (1961).

1000 cm.$^{-1}$ and Δ_2 in the range 3000–10,000 cm.$^{-1}$ then are consistent with the $^4A_{2g}$ ground state for $R_2Co(MNT)_2$ and the $^1A_{1g}$ ground state for $R_2Ni(MNT)_2$.

The electronic spectrum of $R_2Co(MNT)_2$ in the solid or in DMF solution shows a band at 12,500 cm.$^{-1}$ ($\epsilon = 69$), assigned to the $^4A_{2g} \rightarrow {}^4E_g^{(1)}$ ($xz, yz \rightarrow z^2$) transition. This gives $\Delta_3 = 9{,}500$ cm.$^{-1}$. The next band, a shoulder indicative of a maximum at 15,000 cm.$^{-1}$ ($\epsilon \cong 200$), is assigned $^4A_{2g} \rightarrow {}^4E_g^{(2)}$ ($xz, yz \rightarrow xy$), giving $\Delta_2 = 5{,}500$ cm.$^{-1}$, in agreement with the value assumed above for Δ_2. The bands at higher energies are much more intense and probably are due to charge transfer transitions.

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SYNTHESES OF 5-TRIFLUOROMETHYLURACIL AND 5-TRIFLUOROMETHYL-2'-DEOXYURIDINE[1]

Sir:

We wish to report the syntheses of 5-trifluoromethyluracil (VI) ("trifluorothymine") and its deoxyriboside 5-trifluoromethyl-2'-deoxyuridine (VII) which was done in connection with the interest of this laboratory in fluorinated pyrimidines. Replacement of the hydrogen atom of carbon-5 of uracil by fluorine gives 5-fluorouracil,[2] which is incorporated into ribonucleic acid,[3] and inhibits the growth of murine and human tumors as a result of the inhibition of thymidylate synthetase[4] by 5-fluoro-2'-deoxyuridine-5'-monophosphate.[5] Replacement of the same hydrogen atom by chlorine, bromine, or iodine leads to compounds[6] that are incorporated into deoxyribonucleic acid in place of thymine, presumably because of the similarity in sizes of these atoms and the methyl group of thymine. We considered, therefore, that similar effects might be produced by the replacement of the methyl group of thymine by a trifluoromethyl group, which would also have a similar size.

Other trifluoromethylpyrimidines have been prepared recently by Inoue, Saggiomo and Nodiff[7] and by Barone,[8] but the trifluoromethyl group has not been introduced into the crucial 5 position of a pyrimidine.

Trifluoromethylacrylonitrile[9] (I) dissolved in ethanol and saturated with hydrogen bromide at 5° gave β-bromo-α-trifluoromethylpropionamide (II) in 75% yield, m.p. 101–103°. (*Anal.* Calcd. for $C_4H_5NOF_3Br$: C, 21.84; H, 2.29; N, 6.36; F, 25.91. Found: C, 21.99; H, 2.39; N, 6.52; F, 25.77.) Condensation of this bromoamide with a 2 to 4 molar excess of urea in aqueous dioxane at 90° gave the monosubstituted urea (III) in *ca.* 30% yield, m.p. 169–171° (*Anal.* Calcd. for $C_5H_8N_3F_3O_2 \cdot C_2H_5OH$: C, 34.29; H, 5.72; N, 17.14; F, 23.24. Found: C, 33.87; H, 5.18; N, 17.27; F, 23.64). On refluxing this compound in 5 *N* hydrochloric acid, hydrolysis of the amide group first occurred, then cyclization giving the dihydropyrimidine (IV) in 60% yield m.p. 203–205° dec. (*Anal.* Calcd. for $C_5H_5N_2O_2F_3$: C, 33.00; H, 2.77; N, 15.38; F, 31.30. Found: C, 33.11; H, 2.81; N, 15.20; F, 31.26). Treatment of (IV) in acetic acid under reflux with one mole of bromine gave the bromohydropyrimidine (V) in 70% yield, m.p. 218–221° dec., which on heating in dimethylformamide[10] for 1 hour at 140° gave 5-trifluoromethyluracil (VI) in 85% yield, m.p. 239–241° *dec.* (*Anal.* Calcd. for $C_5H_3N_2F_3O_2$: C, 33.35; H, 1.68; N, 15.55; F, 31.65. Found: C, 33.75; H, 1.92; N, 15.40; F, 31.96), pk_a (water) 7.35, (method of Shugar and Fox[11]) Ultraviolet absorption spectra, in 0.1 *N* hydrochloric acid λ_{max} 257 mμ, ε molar 7050; in pH 7.0 buffer, λ_{max} 257 mμ, ε molar 6830; in pH 8.1 buffer λ_{max} 279, ε molar 6900; R_f, butanol/water, 86/14 v./v. ascending 0.79; butanol/acetic acid/water, 50/20/30 v./v., descending 0.80; ethyl acetate/methyl alcohol/water/*n*-heptane, 10/6/5/3 v./v., upper phase[12] 0.76.

The 5-trifluoromethyluracil was converted quantitatively to 5-carboxyuracil in 20 minutes at room temperature in 1.0 *N* sodium hydroxide, and in 24 hours in 0.1 *N* sodium bicarbonate. The lability of the trifluoromethyl group in alkali may prove to be of some interest for chemical mutagenesis since it could be converted to a carboxyl group under conditions which would not degrade deoxyribonucleic acid.

5-Trifluoromethyl-2'-deoxyuridine (VII) has been prepared using a nucleoside phosphorylase preparation[13] from Ehrlich ascites cells, and 2-deoxy-α-D-ribose-1-phosphate. The deoxyribonucleoside was separated from the unconverted 5-trifluoromethyluracil by electrophoresis on paper in borate buffer pH 9.2, and purified by paper chromatography using a butanol/formic acid/water, 77/10/13 v./v., descending solvent system. It was obtained in an over-all yield of 8.2% m.p. 169–172°.

(*Anal.* Calcd. for $C_{10}H_{11}N_2O_5F_3$: C, 40.55; H, 3.73; F, 19.24. Found: C, 40.50, H, 4.15; F, 18.95.) Ultraviolet absorption spectra, in 0.01 *N* hydrochloric acid, λ_{max} 260 mμ, ε molar 9590, in 0.01 *N* sodium hydroxide, λ_{max} 260 mμ, ε molar 6250; R_f butanol/formic acid/water, 77/10/13 v./v., descending 0.72, ethyl acetate/methanol/water/*n*-heptane 10/6/5/3 v./v. descending 0.62.

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