Studies in Non-stoichiometry: Magnetic Susceptibilities in the Tungsten–Oxygen System[1]

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Magnetic susceptibilities have been measured by the Gouy method for several tungsten oxides of the series WO_x. At 297.5°K. the susceptibility per unit volume is found to increase monotonically from -0.65×10^{-6} to $+0.46 \times 10^{-6}$ as x in WO_x decreases from 3 to 2. Results are interpretable in terms of a defect structure in which $3 - x$ oxygen atoms have been removed from a host WO_3 lattice leaving $2(3 - x)$ electrons in the conduction band of the host. Quantitative agreement with a Pauli–Peierls calculation is surprisingly good. The model may be applicable to other non-stoichiometric oxides for which "mixed-oxidation-state" structures have been postulated.

Like most of the other transition elements, tungsten can form a series of oxides which do not conform to simple Daltonian stoichiometry. Traditionally, these non-stoichiometric oxides have been interpreted as mixtures of several oxidation states. Magnéli, however, has shown[2] that the crystal structures of the tungsten–oxygen series are rather simply related and are differentiated from each other principally in the relative number of WO_6 octahedra that are mutually corner-linked or edge-linked. In WO_3, the WO_6 octahedra are joined through sharing of corner oxygen atoms only; in WO_2, the WO_6 octahedra share edges so as to give the extended chains of the rutile structure. Between these terminal compounds, Magnéli finds a series of oxides W_nO_{3n-1} in which there are "slabs" of WO_6 octahedra connected through corner-sharing but with the "slabs" joined to each other by edge-sharing. As n increases, the size of the "slabs" is believed to be larger. In a series of extended solid state structures such as W_nO_{3n-1}, the concept of pentavalent and tetravalent tungsten loses utility since the local symmetry about each tungsten atom is identically octahedral. A similar problem with the alkali metal–tungsten bronzes was resolved successfully[3] by replacing hypothetical pentavalent tungsten in $xMW^VO_3 \cdot (1-x)W^{VI}O_3$ by an electron gas formed from the valence electrons of ionized M atoms in $M_xW^{VI}O_3$. In investigating the properties of WO_3 doped with various metals we speculated on the possibility that the non-stoichiometric oxides WO_x might also be interpretable in terms of an electron gas—specifically, that they are defect structures in which $3-x$ oxygen atoms have been removed from a WO_3 host lattice leaving $2(3-x)$ electrons in the host conduction band. In this communication we report some magnetic measurements and their interpretation by such a model. Electrical characteristics, more difficult to determine since they require single crystals for unambiguous interpretation, are currently under investigation in this Laboratory and, although the work is by no means complete, at least the results are not inconsistent with the model used in this paper.

(1) This research was supported by the United States Air Force under Contract No. AF 49 (638)-191 and was monitored by the Air Force Office of Scientific Research and Development Command through its Directorate of Solid State Sciences.

(2) A. Magnéli, Nova Acta Reg. Soc. Sci., Upsala, 1949, Ser. IV, 14, No. 8; Acta Cryst., 6, 495 (1953); J. Inorg. Nuclear Chem., 2, 330 (1956); Acta Chem. Scand., 9, 1382 (1955).

(3) L. E. Conroy and M. J. Sienko, J. Am. Chem. Soc., 74, 3520 (1952); F. Kupka and M. J. Sienko, J. Chem. Phys., 18, 1296 (1950).

Experimental Procedure and Results

Preparation of Samples.—Tungsten powder and tungsten trioxide powder of at least 99.9% purity were thoroughly ground up as mixtures corresponding to $WO_{2.00}$, $WO_{2.50}$, $WO_{2.75}$, and $WO_{2.875}$—i.e., $n = 1, 2, 4$ and 8 in the series W_nO_{3n-1}. They were fired for 40 hr. under argon at 1000° until X-ray analysis showed complete absence of tungsten or β-tungsten lines. Longer heating with and without subsequent regrinding gave no change in the X-ray pattern. Chemical composition was checked by firing aliquots in oxygen to complete oxidation to WO_3. The weight increase due to oxygen up-take was within 1% of that calculated assuming complete conversion of the starting mixtures to homogeneous WO_x. In the case of WO_2, an additional check was made by comparing our observed X-ray spacings with the interplanar distances calculated from the data of Magnéli.[4] Agreement was very good.

Densities.—Densities were determined pycnometrically using water as the immersion liquid. Within the limits of experimental error, ± 0.01 g./cc., there was no difference in the density measured on powder portions or chunks of the products. The measured densities in g./cc. are: $WO_{2.00}$, 11.15; $WO_{2.50}$, 8.26; $WO_{2.75}$, 7.74; and $WO_{2.87}$, 7.30.

Magnetic Measurements.—Magnetic susceptibilities were determined using the Gouy technique with semi-micro balance and electromagnet as previously described.[5] Because of changes in the design of the power supply to the magnetic field, it was necessary to re-calibrate the field using a 30% "special low cobalt" nickel chloride solution. A check on powdered NaCl gave a measured molar susceptibility of -28.5×10^{-6} compared to the best literature value of -30.2×10^{-6}. Calibration and the measurements were all carried out at 24.5°, except for one sample of WO_2 which in addition was taken down to liquid nitrogen temperature but without sensible effect. For each oxide composition, three samples were selected from different, independent preparations and measured nine times, corresponding to three packings each at three re-alignments in the field. Results are quoted in Table I as volume susceptibilities. They are true volume susceptibilities in the sense that they are calculated from an "apparent volume susceptibility," obtained from the measured weight change, by multiplying it with the ratio "true density/apparent density of powder." The apparent density of the powder was figured from the cathetometrically measured height of powder in the precision-bore sample tube. Probable errors, which were calculated from a statistical analysis of the 27 measurements on the 3 samples, are rather high because the forces involved here are extremely small. In all cases, measurements were checked at both 3500 and 5000 gauss to monitor independence of field strength and to ensure absence of trace ferromagnetic impurities. The last column in Table I gives the susceptibility per gram-formula weight for the simplest formulas as given.

Discussion

The magnetic susceptibilities of the tungsten oxides show two features of special interest: (a) the susceptibilities are extraordinarily low, much lower than one would normally anticipate for mixtures of W^{+6} with W^{+4} or W^{+5} and (b) the

(4) A. Magnéli, Arkiv Kemi, Min. Geol., 24A, 1 (1947).

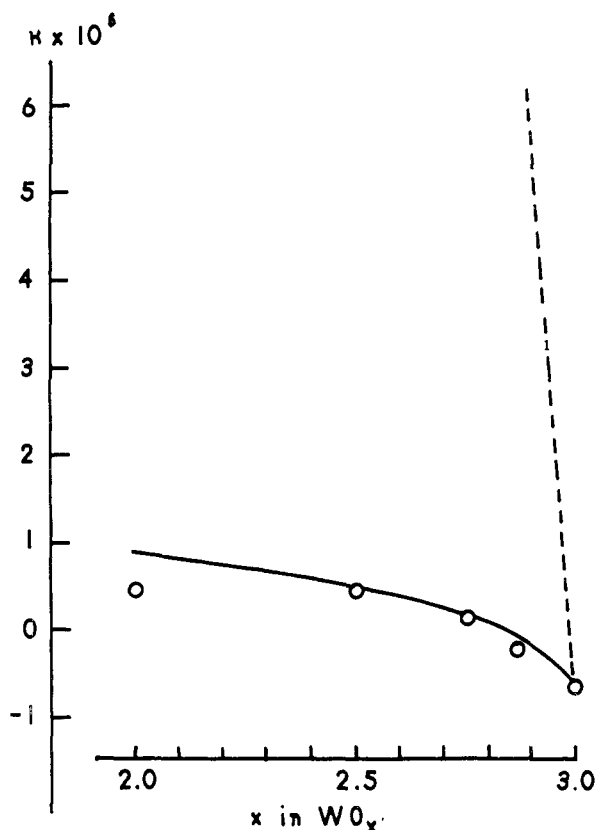(5) J. L. Kernahan and M. J. Sienko, J. Am. Chem. Soc., 77, 1978 (1955).

$H \times 10^{6}$

Fig. 1.—Magnetic susceptibility per cc. as a function of tungsten oxide composition: ---------, localized electrons without exchange demagnetization; ———, quasi-free electrons; O, observed susceptibilities.

maximum at $WO_{2.50}$ in the molar susceptibility is not duplicated in the volume susceptibility. This combination of features along with low electrical resistivities as reported by Glemser and Sauer[6] strongly suggest that a model based on delocalized electrons, perhaps like the degenerate electron gas used for the tungsten bronzes, is more appropriate for describing the tungsten oxides than is the traditional "mixed-oxidation-state" model. With a

TABLE I

EXPERIMENTAL MAGNETIC SUSCEPTIBILITIES OF TUNGSTEN OXIDES

Oxide	κ, susceptibility per cc.	Probable error	χM, susceptibility per mole
$WO_{2.00}$	0.456×10^{-6}	$\pm 0.026 \pm 10^{-6}$	8.83×10^{-6}
$WO_{2.50}$	$.405 \times 10^{-6}$	$\pm .032 \times 10^{-6}$	11.0×10^{-6}
$WO_{2.75}$	$.138 \times 10^{-6}$	$\pm .016 \times 10^{-6}$	4.06×10^{-6}
$WO_{2.87}$	$- .226 \times 10^{-6}$	$\pm .024 \times 10^{-6}$	$- 7.11 \times 10^{-6}$
$WO_{3.00}$	$- .649 \times 10^{-6}$	$\pm .054 \times 10^{-6}$	-21.0×10^{-6}

mixture of oxidation states, one would have to attribute observed low magnetic susceptibilities to exchange demagnetization. However, exchange demagnetization has not proved particularly fruitful as a way of accounting *quantitatively* for observed electric, magnetic and chemical properties of non-stoichiometric compounds. In general, a searching quantitative test has not been possible because there are difficulties in calculating exchange

(6) O. Glemser and H. Sauer, *Z. anorg. Chem.*, **252**, 144 (1943).

integrals for structures that place so many parameters at our disposal, not the least of which is the variation in chemical composition. Furthermore, the mechanism by which "exchange demagnetization" is set up is still not certain and may call for ferromagnetic ordering at least as frequently as the antiferromagnetic ordering that would intuitively follow from a "covalent bonding" model. In this paper, although we considered exchange demagnetization as a possible explanation of our results, we quickly gave it up because it did not allow us to calculate in closed form the magnetic susceptibility of tungsten oxide at any composition and also because it seemed to predict a dependence on concentration that was directly opposite to the experimentally observed.

Two extreme models can be proposed for the tungsten oxides. In one, which we call the Langevin model, the lower oxides are viewed as containing W^{+5} or W^{+4}—*i.e.*, with one or two, respectively, electrons bound to local centers and giving rise to magnetic moments appropriate to d^{1} or d^{2} configurations. In the alternate model, which we call the Pauli–Peierls model, the lower oxides are viewed as containing essentially free electrons in a WO_{3} lattice—*i.e.*, a collective electron assembly in which only the electrons at the top of the distribution can orient in a magnetic field and thereby contribute to the moment. Figure 1 shows as a function of tungsten oxide composition a comparison of the volume susceptibilities as calculated by these two models with the experimentally observed values. The dashed curve represents magnetic susceptibilities calculated on the Langevin model; the solid curve represents the susceptibilities assuming quasi-free electrons as in the Pauli–Peierls calculation; the circles represent the observed susceptibilities. The agreement is much better with the Pauli–Peierls model and, considering the simplicity of the calculation, is truly remarkable.

In calculating predicted susceptibilities we have had to face two problems: (1) What is an appropriate value for the diamagnetic susceptibility correction of the oxide anion in the structure and, concomitantly, what is an appropriate value for the temperature-independent paramagnetism of the tungsten cation? (2) What is an appropriate value for the effective mass of an electron if it is "quasibound" in an oxide host of variable composition?

The diamagnetic increment of oxide anion ranges from -4.6×10^{-6} as recommended by Pascal[7] in his remarkably successful scheme for organic compounds to -20×10^{-6} as quoted by Klemm[8] for gaseous oxide ion. We have selected -9.8×10^{-6} on the basis of a graphical extrapolation of the isoelectronic sequence Mg^{++}, Na^{+}, F^{-}, O^{--}. The Brindley and Hoare diamagnetic increments for Mg^{++}, Na^{+} and F^{-} (based on their additivity analyses of crystals[9]) were plotted as a function of the square of the ionic radii and extrapolated to

(7) See, for example, P. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956.

(8) Landolt–Börnstein, "Zahlenwerte und Funktionen," Band I, Teil 1, p. 396.

(9) See the review paper of W. R. Myers, *Rev. Mod. Phys.*, **24**, 15 (1952), for a comparison of diamagnetic increments.

the ionic radius of $O^=$. The justification for this procedure is that the diamagnetic moment is proportional to the electron density as r^2 with the major contribution coming from the outermost reaches of the ion. A somewhat better fit between experiment and the Pauli–Peierls calculation can be obtained using the Pascal value of -4.6×10^{-6} for $O^=$. (However, there is an almost limitless number of combinations, many of which would improve the fit with experiment, but the choice of diamagnetic increment would have to be justified a posteriori, perhaps validly only for the tungsten–oxygen system.) Using -9.8×10^{-6} for $O^=$ and -21.0×10^{-6} as the best value for the molar susceptibility of WO_3, we calculate $+8.4 \times 10^{-6}$ as the combined diamagnetic increment and high-frequency, temperature-independent paramagnetism of W^{+6}. In Table II we show the breakdown of a Langevin type calculation assuming the tungsten oxides are appropriate mixtures of W^{+4}, W^{+5} or W^{+6}. For W^{+4} we have used 1100×10^{-6} for the molar susceptibility; for W^{+5}, 1020×10^{-6}. These values are for d^2 and d^1 configurations, respectively, and are little changed if we were to go over to a spin-only calculation or if we consider octahedral field-splitting of a $^3F(d^2)$ or a $^2D(d^1)$ configuration. It is evident from comparison of the last column of Table II with the first column of Table I that a simple bound-electron-model will not work for the tungsten oxides unless exchange demagnetization is essentially complete. In the latter event, we need to face the question as to how there can be any rise in κ at all in going from WO_3 to WO_2. We would expect more perfect demagnetization as we decrease average interatomic spacing between magnetic centers with perhaps incipient ferromagnetic ordering near WO_3, not near WO_2.

TABLE II

CALCULATED MAGNETIC SUSCEPTIBILITIES ON LANGEVIN MODEL

Oxide	Equivalent composition	Calculated κ, per cc.
$WO_{2.00}$	$W^{IV}O_2$	$+56.2 \times 10^{-6}$
$WO_{2.50}$	$W^VO_{2.5}$	$+37.0 \times 10^{-6}$
$WO_{2.75}$	$(0.5W^VO_{2.5})(0.5W^{VI}O_3)$	$+16.7 \times 10^{-6}$
$WO_{2.87}$	$(0.26W^VO_{2.5})(0.74W^{VI}O_3)$	$+ 7.8 \times 10^{-6}$
$WO_{3.00}$	$W^{VI}O_3$	$- 0.65 \times 10^{-6}$

The Pauli–Peierls calculation, which incidentally has a built-in exchange demagnetization in the electron-pairing that exists in all states except those near the top of the Fermi distribution, is shown in breakdown in Table III. The columns headed "moles per cc." are calculated from the observed densities and the gram-formula-weights of the various oxides. The "moles per cc." of electrons are calculable as twice the difference between theoretical oxygen as if the material were WO_3 and actual oxygen per cc. of material. It amounts to pulling neutral oxygen atoms out of a WO_3 lattice, leaving behind two electrons per oxygen, until the composition WO_x is attained. The columns headed "susceptibility per cc." are calculated applying $+ 8.4 \times 10^{-6}$ per mole of tungsten atoms and -9.8×10^{-6} per mole of oxygen atoms. For the

TABLE III

CALCULATED MAGNETIC SUSCEPTIBILITIES ON PAULI-PEIERLS MODEL

	Moles per cc.			Susceptibility per cc. ($\times 10^6$)			
	Tungsten	Oxygen	Electrons	Tungsten	Oxygen	Electrons	Total
$WO_{2.00}$	0.0517	0.103	0.103	0.43	-1.01	1.51	0.93
$WO_{2.50}$	.0369	.0923	.0369	.31	-0.91	1.07	.47
$WO_{2.75}$	.0340	.0935	.0170	.29	$- .92$	0.83	.20
$WO_{2.87}$	.0318	.0913	.00827	.27	$- .90$	0.65	.02
$WO_{3.0:}$	.0309	.0927	.....	.26	$- .91$	..	$- .65$

electrons, we have used the Pauli–Peierls equation[10]

$$\kappa = \frac{4m^*\mu_0^2}{h^2}(3\pi^2 n)^{1/3}\left(1 - \frac{m^2}{3m^{*2}}\right)$$

where m^* is the effective mass of the electrons, μ_0 is the Bohr magneton, n is the electron density per cc., m is the rest mass of the electron and h is the Planck constant. For the effective mass of the electrons, we have used 1.9 times the rest mass, this being a mean of the experimental values found in the alkali tungsten bronzes.[11] Because the tungsten oxides are not cubic, whereas the derived effective mass was deduced for cubic structures, one could argue that the single scalar effective mass should be replaced by a tensor, which would mean that the electronic contribution to the magnetic susceptibility would not be isotropic. However, any anisotropy would not have been detected in the powder measurements.

Comparison of the last column of Table III with the first column of Table I shows satisfying agreement. The agreement can be made even better by making other choices for the magnetic increments of $O^=$ and W^{+6}. Furthermore, it is quite probable that one single value of the effective electron mass should not be used for the whole range of composition possible with WO_x. As discussed for the alkali tungsten bronzes M_xWO_3 there is theoretical and experimental justification[11] for believing that the effective mass of the electrons increases as states are removed from the conduction band by local polarization of tungsten atoms by M^+ ions. In WO_x, when x is near 3, any oxygen defect probably puts electrons into the conduction band with fairly low effective mass, though there may be a finite trapping energy at the site of the oxygen defect. As the deviation from WO_3 stoichiometry increases, there is probably increase in the electron effective mass at least until the trapping sites effectively begin to overlap. On the basis of arguments previously given for M_xWO_3, we might expect overlap of the trapped electrons to begin to occur when 0.26 moles of oxygen have been removed, corresponding to $WO_{2.74}$. With x less than 2.74 we would expect local polarization to be reduced and the effective mass to be decreased nearer to the free electron value. Such behavior would effectively pull down the two extremes of the solid curve shown in Fig. 1.

Other transition metal oxides, particularly VO_x[12] and NbO_x[13] show higher magnetic susceptibilities

(10) See, for example, A. H. Wilson, "The Theory of Metals," 2nd Ed., Cambridge University Press, Cambridge, 1954, p. 155.

(11) M. J. Sienko and Thu Ba Nguyen Truong, J. Am. Chem. Soc., 83, 3939 (1961).

(12) E. Hoschek and W. Klemm, Z. anorg. Chem., 242, 63 (1939).

(13) G. Brauer, ibid., 256, 10 (1948).

and also maxima in their molar susceptibilities as x is decreased below 2.5. These maxima may be symptomatic of the occurrence of electron trapping sites at oxygen defects. The greater the trapping energy, the more firmly bound the electron and the bigger its contribution to the paramagnetic susceptibility. The sketchy data that are available, particularly for the series VO_x, NbO_x, TaO_x and CrO_x, MoO_x, WO_x, suggest a decreasing maximum in the susceptibility *vs.* composition curves near 2.4 and 2.8, respectively. Otherwise, the susceptibilities can be interpreted at least qualitatively in terms of a partially-delocalized-electron model on either side of the maxima. It would be most useful to have additional magnetic data on other non-stoichiometric oxides and also electrical conductivity measurements over the range of composition.
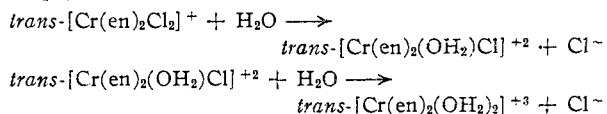

Kinetics and Products of Aquation of *cis*- and *trans*-Dichlorobis-(ethylenediamine)-chromium(III) Cations[1a,b]

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The products of the first-stage aquation of *trans*-$[Cr(en)_2Cl_2]^+$ in $0.10 f$ HNO_3 at $35.0°$ in the absence of light were found to be *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ and a dichloro complex tentatively identified as *trans*-$[Cr(en)-(OH_2)_2Cl_2]^+$ (*i.e.*, 1,6-dichloro-2,3-diaquo-ethylenediamine-chromium(III) cation). These previously unisolated or unreported chloroaquo complexes have been isolated in solution and their visible absorption spectra determined. Pseudo first-order rate constants for formation of these products are $(6.90 \pm 0.41) \times 10^{-5}$, $(1.12 \pm 0.40) \times 10^{-5}$ and $(0.78 \pm 0.05) \times 10^{-5}$ sec.$^{-1}$, respectively. The only detectable first-stage aquation product of *cis*-$[Cr(en)_2Cl_2]^+$ in $0.10 f$ HCl at $35.0°$ in the dark was *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$, formed directly with a pseudo first-order rate constant of $(1.11 \pm 0.02) \times 10^{-3}$ sec.$^{-1}$. Isomerization of *cis*-$[Cr(en)_2Cl_2]^+$ and of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ to the *trans* isomers was not detected, conservative upper limits thus established for the *cis*-to-*trans* isomerization rate constants being 5×10^{-6} and 2×10^{-5} sec.$^{-1}$, respectively. The possibility of *trans*-to-*cis* isomerization of these two complexes could be neither confirmed nor ruled out, but $k \leqslant 1.12 \times 10^{-5}$ sec.$^{-1}$ for isomerization of *trans*-$[Cr(en)_2Cl_2]^+$ and $k < 1 \times 10^{-5}$ sec.$^{-1}$ for isomerization of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$.

This investigation began in a study of the kinetics of production of ionic chloride from *trans*-dichlorobis-(ethylenediamine)-chromium(III) cation in acidic aqueous solution,[2] as part of a program of comparing the reaction kinetics of analogous chromium(III) and cobalt(III) complexes. At first it was thought that a simple two-step process such as

$$trans\text{-}[Cr(en)_2Cl_2]^+ + H_2O \longrightarrow$$
$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + Cl^-$$
$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + H_2O \longrightarrow$$
$$trans\text{-}[Cr(en)_2(OH_2)_2]^{+3} + Cl^-$$

might account for the production of ionic chloride (*i.e.*, chloride ions displaced from the complex) during aquation, but the experimental kinetic data on the secondary aquation soon revealed that the actual process must be more complicated. Therefore we undertook to separate and identify the reaction products at various reaction times during the aquation of both *trans*- and *cis*-$[Cr(en)_2Cl_2]^+$. Combination of the chromatographic separation data with determinations of the total rate of loss of the reactant complex ion and the rate of production of ionic chloride, together with spectral observations, have enabled us to evaluate or place upper limits on nine rate constants for reactions occurring in the primary aquation of *trans*- and *cis*-$[Cr(en)_2Cl_2]^+$ and the rearrangements of these two cations and their first-stage aquation products. In favorable cases, this approach can provide a knowledge of the steric course of the aquation, needed for a full understanding of the reaction mechanism, and can lead to the discovery of reaction paths which are not revealed by studies of the rate of production of ionic chloride alone. Earlier kinetic studies[3,4] of the aquation of *trans*- and *cis*-$[Cr(en)_2Cl_2]^+$, including our own,[2] were based solely on measurement of the rate of chloride-ion release, and as is true of many previous kinetic studies of the aquation of coördination complexes, did not include identification of the product complexes.

Experimental

trans-Dichlorobis-(ethylenediamine)-chromium(III) Nitrate.—This compound was prepared and characterized as described in a previous paper.[2]

cis-Dichlorobis-(ethylenediamine)-chromium(III) Chloride Hydrate.—Violet powdered anhydrous chromium(III) chloride, donated by the Diamond Alkali Company, was suspended in technical ethyl ether and mixed with a 20% excess (in 20% ethereal solution) of Eastman Kodak "White Label" ethylenediamine (dried by distillation from sodium hydroxide). After ~2 hr. on the steam-bath, the mixture formed yellow-brown fluffy tris-(ethylenediamine)-chromium(III) chloride, which was washed with ethyl ether and dried overnight at ~100°; yield~100%. This crude product was recrystallized with half its weight of ammonium chloride from $1 f$ HCl. The crystals were filtered, rinsed with ethyl ether, then thermally decomposed[5] in an Abderhalden drier at the temperature of refluxing methyl salicylate (b.p. 220–224°); concd. H_2SO_4 was used to absorb the ethylenediamine evolved. The resulting crude *cis*-dichlorobis-(ethylenediamine)-chromium(III) chloride was recrystallized twice from 3–6 f HCl solution; yield ~20%.

(1) (a) Based on a portion of the doctoral dissertation of D. J. MacDonald, University of California, Los Angeles, January, 1960. (b) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University. (c) California Research Corp., Richmond, Calif.

(2) D. J. MacDonald and C. S. Garner, *J. Inorg. Nuclear Chem.*, 18, 219 (1961).

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(4) R. G. Pearson, R. A. Munson and F. Basolo, *ibid.*, 80, 504 (1958).

(5) C. L. Rollinson and J. C. Bailar, Jr., "Inorganic Syntheses," Vol. II, W. C. Fernelius, ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 201.