The dihydrate heated *in vacuo* for 6 hr. at 58° yielded the anhydrous compound, a purple crystalline material.

Anal. Calcd. for $Co(C_5H_7O_2)_2$: Co, 22.94; C, 46.71; H, 5.48. Found: Co, 22.8; C, 46.89; H, 5.56.

Bis-(salicylaldehyde)-Co(II).—The procedure of Tyson and Adams[18] led to an orange crystalline product, the dihydrate.

Anal. Calcd. for $Co(C_7H_5O_2)_2·2H_2O$: Co, 17.48; C, 49.85; H, 4.18. Found: Co, 17.2; C, 49.97; H, 4.48.

By heating the dihydrate *in vacuo* for 12 hr. at 58°, the brown crystalline anhydrous compound was obtained.

Anal. Calcd. for $Co(C_7H_5O_2)_2$: Co, 19.57; C, 55.81; H, 3.35. Found: Co, 19.6; C, 55.71; H, 3.61.

Bis-(benzoylacetonato)-Co(II).—The compound was reported previously by Musante.[19] The orange-brown product was obtained by direct reaction of an aqueous solution of Co(II) acetate with an ethanolic solution of benzoylacetone; it was recrystallized twice from methanol–water to give yellowish crystals which readily lost water on standing. These crystals were completely dehydrated to the dark brown anhydrous compound by heating *in vacuo* at 80° for 24 hr.

Anal. Calcd. for $Co(C_{10}H_9O_2)_2$: Co, 15.46; C, 63.00; H, 4.76. Found: Co, 15.5; C, 62.95; H, 4.72.

Bis-(ethylbenzoylacetato)-Co(II).—Cobalt(II) acetate tetrahydrate (12.5 g.) was dissolved in 100 ml. of 50% ethanol to which was then added 19.1 g. of ethylbenzoylacetate. 3 *N* ammonia was added slowly until the solution was slightly basic. A yellowish product precipitated which was filtered off, washed well with water and ethanol and air-dried giving a light yellow powder.

Anal. Calcd. for $Co(C_{11}H_{11}O_3)_2·2H_2O$: Co, 12.35; C, 55.35; H, 5.49. Found: Co, 12.3; C, 55.31; H, 5.58.

Heating *in vacuo* at 80° for 4 hr. produced the violet-brown anhydrous compound.

Anal. Calcd. for $Co(C_{11}H_{11}O_3)_2$: Co, 13.35; C, 59.87; H, 5.02. Found: Co, 13.1; C, 59.75; H, 4.93.

Bis-(guaiacolato)-Co(II).—The compound has been mentioned previously by Mellor and Craig.[20] 6.2 g. of cobaltous acetate tetrahydrate was dissolved in 100 ml. of 50% ethanol. To this solution was added 6.2 g. of guaiacol (*o*-methoxyphenol) in 100 ml. of ethanol and 6 *N* NH_3 was added slowly with stirring as a granular precipitate formed. The purple product was filtered off, washed well with water and ethanol and dried *in vacuo*.

Anal. Calcd. for $Co(C_7H_7O_2)_2$: Co, 19.31; C, 55.10; H, 4.62. Found: Co, 19.2; C, 54.96; H, 4.81.

Bis-(hexafluoroacetylacetonato)-Co(II) Hydrate.—The compound was obtained by direct reaction of an aqueous solution of cobaltous acetate with an ethanolic solution of hexafluoroacetylacetone. The orange crystalline product was twice recrystallized from ethanol–water.

Anal. Calcd. for $Co(C_5HF_6O_2)_2·5/2H_2O$: Co, 11.36; C, 23.18; H, 1.36. Found: Co, 11.1; C, 23.10; H, 1.78.

The hydrate could not be dehydrated by heating *in vacuo* at 100° for 24 hr.

Bis-(trifluoroacetylacetonato)-Co(II).—The hydrate was obtained by a direct reaction similar to that used to prepare the hydrate of the hexafluoro compound.

Anal. Calcd. for $Co(C_5H_4F_3O_2)_2·5/2\ H_2O$: Co, 14.37; C, 29.28; H, 3.19. Found: Co, 14.0; C, 29.48; H, 3.46.

The anhydrous compound was obtained from the hydrate as previously described.[16]

Bis-(tropolonato)-Co(II).—Tropolone was prepared according to the method of Doering and Knox.[21] The crude product was sublimed, m.p. 48–49°, lit. 49°; 1.06. g. of cobaltous acetate tetrahydrate was dissolved in 20 ml. of water and added slowly to a solution of 1.04 g. of tropolone in 30 ml. of 50% ethanol. A blood red precipitate formed which was filtered off, washed carefully with water, a small amount of 50% ethanol, ether and air-dried.

Anal. Found: C, 52.97; H, 3.69; corresponding closely to the monohydrate. Calcd. for $Co(C_7H_5O_2)_2·H_2O$: C, 52.68; H, 3.79.

This product was dried *in vacuo* at 58° for three days to give the deep red anhydrous compound.

Anal. Calcd. for $Co(C_7H_5O_2)_2$: C, 55.81; H, 3.25. Found: C, 55.77; H, 3.59.

Co(II) Kojate.—The compound was reported previously by Wiley, *et al.*[22]; 4.4 g. of cobaltous acetate tetrahydrate was dissolved in 25 ml. of water and to this solution was added 5 g. of sublimed kojic acid in 40 ml. of 50% ethanol. An orange precipitate slowly appeared. The solution was allowed to stand for 24 hr.; the orange product was filtered and washed thoroughly with water, ethanol and ether. A light orange powder resulted, insoluble in common noncoördinating solvents.

Anal. Found: C, 41.49; H, 3.29; Co, 16.5; agreeing best with $Co(C_6H_5O_4)_2·1/_2H_2O$ for which, calcd.: C, 41.16; *H, 3.17; Co, 16.76.*

The water could not be removed by heating *in vacuo* at 100° for 24 hr.

Acknowledgments.—We are grateful to the National Science Foundation and the U. S. Atomic Energy Commission (Contract AT(30-1)-1956) for financial support and to the General Electric Company for a Charles Coffin Fellowship to R. H. H.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS]

Magnetic Evidence Indicative of Structures and Structural Changes in Complexes of Cobalt(II)

BY F. A. COTTON AND R. H. HOLM

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It is observed that the literature now contains data and generalizations relating to the magnetic properties of a number of basic kinds of cobaltous complexes. It is shown that in this context magnetic data reported for bis-(*p*-toluidine)-cobalt(II) thiocyanate as a solid and in several solvents and for several isonitrile complexes of Co(II) can be used to infer certain features of stereochemistry and changes in stereochemistry of these substances.

Recent studies in this Laboratory have established that the magnetic behavior of tetrahedral cobaltous complexes is in good accord with the general pattern to be expected from ligand field theory and, furthermore, semi-quantitative correlations have been established between magnetic moments of such complexes and the positions of the ligands in the spectrochemical series.[1,2] It has

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TABLE I

STRUCTURES AND MAGNETIC MOMENTS OF REPRESENTATIVE HEXACOÖRDINATED COMPLEXES OF Co(II)

Compound	Structure[a]	Magnetic moment, B.M.[a,b]
$CoCl_2$	CdI_2 structure with CoX_6 octahedra[4]	$5.29\ (\theta = +38)$[5]
$CoBr_2$	CdI_2 structure with CoX_6 octahedra[4]	$5.2\ (\theta = -6)$[6]
CoI_2	CdI_2 structure with CoX_6 octahedra[4]	$5.0\ (\theta = +5)$[7]
CoO	NaCl structure; Co(II) is 6-coördinated[4]	$4.92\ (\theta = -280)$[8]
$Co(OH)_2$	CdI_2 structure with $Co(OH)_6$ units[4]	$4.88\ (\theta = -1)$[9]
$CoCl_2\cdot 6H_2O$	Contains *trans*-$[Co(H_2O)_4Cl_2]$ units[10]	4.94[c,11]
$(NH_4)_2Co(H_2O)_6(SO_4)_2$	Slightly tetragonal $Co(H_2O)_6$ units[12–14]	5.12[d] $(\theta = -27)$[15]
$Co(H_2O)_6(ClO_4)_2\cdot 6H_2O$	$Co(H_2O)_6^{+2}$ ions	4.93[11]
$CoCl_2(py)_4$[e]	*trans*-CoN_4Cl_2 units as in Ni complex[17]	4.85[c,18]
$Co(OCOCH_3)_2\cdot 4H_2O$	Tetragonal CoO_6 units as in Ni salt[19]	5.16[c,f]
$KCo(II)[Co(III)(CN)_6]$	Contains octahedral $Co(II)N_6$ units[20]	5.30[c,20]
$K_2Co(II)[Fe(II)(CN)_6]$	Contains octahedral $Co(II)N_6$ units[20]	4.90[c,20]
$Co[SC(NH_2)_2]_4Cl_2$	*trans*-CoS_4Cl_2 units as in Ni complex[21]	4.90[c,f]

[a] References indicated. [b] θ is Weiss constant in the expression $\mu(\text{B.M.}) = 2.84\sqrt{\chi_M(T - \theta)}$. [c] Calculated from susceptibility at room temperature only. [d] Calculated from χ_M at 300° and θ. [e] py = pyridine. [f] Measurement made by present authors.

also been found that a number of planar, quadricoordinate, spin-free Co(II) complexes all have moments in the range 4.8–5.2 B.M.,[3] and this has been explained on the basis that in complexes of this type the ground electronic state of the Co(II) ion has intrinsic orbital degeneracy thus giving a substantial orbital contribution to the moment which is largely independent of the strength of the ligand field.[3]

To complete the necessary basis for interpretation of some new results to be reported here and others already in the literature, we must also consider the magnitudes of the moments to be expected in three other types of Co(II) complexes, *viz.*, (1) spin-paired square, quadricoördinate species, (2) spin-paired octahedral species and (3) spin-free octahedral species. For the last of these, data available in the literature together with a few observations of our own afford satisfactory evidence. Such data for complexes whose structures are known are collected in Table I. Additional data for other hexacoördinated complexes of this type are available elsewhere.[22,23] It will be seen that these complexes, like the spin-free planar species, have moments in the range 4.8–5.3 B.M., there being no evident correlation between the room temperature moments and the relative strengths of the ligand fields.

Spin-paired complexes of both planar and octahedral types have been discussed already by Figgis and Nyholm,[24] who concluded from a survey of data available in the literature that for spin-paired square complexes the moments often had very high orbital contributions and ranged from 2.1 to 2.9 B.M., while for spin-paired octahedral complexes, orbital contributions were generally low, moments falling in the range 1.7–2.0 B.M.

A substance to which the magnetic criteria outlined above may be applied is bis-(*p*-toluidine) cobalt(II) thiocyanate. In the solid state this compound is pink, insoluble in most common solvents, and the cobalt ion has a moment of 4.93 B.M. This moment is quite incompatible with the existence of tetrahedral monomeric molecules in the crystal, for which a moment in the range 4.5–4.6 B.M. might be expected on the basis of the results given in refs. 1 and 2. The pink color is indicative of octahedrally coördinated Co(II) and the reflectance spectrum reveals a weak band at 470 mμ, typical of octahedral Co(II). Moreover the infrared spectrum has a band at 2145 cm.$^{-1}$ which is believed to be diagnostic of bridging-SCN-groups.[25] Hence the structure is very probably polymeric octahedral, similar to the structures known to exist in $Cd[SC(NHCH_2)_2]_2(NCS)_2$,[26] $Ni(NH_3)_2(NCS)_2$[27] and $M^{II}(py)_2(NCS)_2$ (M^{II} = Ni, Co),[28] for example. In solution in dimethylformamide the moment was found to be 4.88 B.M. The difference between this and 4.93 B.M. is within the sum of the experimental uncertainties in both figures, but the observed deep blue color of the solution suggests that it must now

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be explained in terms of a different structure. The spectrum of the solution shows an intense band at 630 mμ (and also a much weaker shoulder at 505 mμ) which closely resembles the spectrum observed[29] for the $Co(NCS)_4^{-2}$ ion. We therefore conclude that on dissolution in dimethylformamide, there has occurred a rearrangement to give an ionic substance consisting of $Co(NCS)_4^{-2}$ and a solvated octahedral cation (which may be responsible for the absorption at 505 mμ). The moment of the $Co(NCS)_4^{-2}$ anion is 4.50 B.M.[2] and the root mean square of 4.50 and 5.22, which is a reasonable value for an octahedral complex cation of Co(II), is 4.88, the observed mean moment. A solution of $(p\text{-}CH_3\text{-}C_6H_4NH_2)_2Co(NCS)_2$ in acetonitrile is also blue with an absorption band at 620 mμ. The moment, however, is 4.62 B.M. which is quite close to what we might expect[1,2] for a $Co–N_4$ type tetrahedral complex; hence, we conclude that the complex is tetrahedral and non-ionic in acetonitrile. Several similar observations for bis-(aniline)-$Co(NCS)_2$ have been reported by Nyholm.[30]

A considerable number of isonitrile complexes of Co(II) are known[31] and magnetic data have been reported for many of them. In the course of reporting and suggesting an interpretation for some new data on such compounds, we shall also briefly analyze these previously reported data, all of which are cited by Malatesta in his excellent review.[31] The known complexes usually are of three stoichiometric types: $(RNC)_5\text{-}Co(ClO_4)_2$, $(RNC)_4CoX_2$ and $(RNC)_2CoX_2$. Of the first type, little can be said here; four examples are reported, namely, those in which R is *o*-tolyl, *p*-tolyl, phenyl and methyl. All are paramagnetic in the solid with moments of ~1.75 B.M. at 293°K.; the methyl compound also exhibits a diamagnetic solid modification. These moments provide no basis for any positive conclusion as to the structural nature of the substances. They do, however, militate against the hypotheses of either planar or tetrahedral $Co(RNC)_4^{+2}$ ions being present.

Malatesta[31] lists magnetic data for 18 complexes of the second type. For most of them there is a solid form which has a moment in the range 1.70–1.87 B.M.; the exceptions have moments of 1.57, 1.65, 1.99 and 2.18 B.M. We have obtained these figures by using Curie's law and correcting the susceptibilities listed for diamagnetism.[31] According to the criteria of Figgis and Nyholm,[24] these results might imply that in all cases, except perhaps one, the cobaltous ions are six-coördinated in the solid. The unusual case is that of $(PhNC)_4CoCl_2$ for which an uncorrected moment of 3.27 B.M. is reported. This value does not seem reconcilable with any reasonable structure for the substance and a reinvestigation would seem desirable. Also many of the 18 compounds mentioned above exist also in a second form. In some cases this second form is reported to be diamagnetic which must mean that by some mechanism there is spin pairing between cobalt ions. In others, weak paramagnetism, ranging from 100–200 × 10^{-6} c.g.s.u., is reported for the second isomer. The significance of this remains completely obscure on the basis of present knowledge. It would appear that these $(RNC)_4CoX_2$ compounds must be further investigated before they can be understood and such work has been undertaken.

It is the $(RNC)_2CoX_2$ compounds which are of principal concern to us. Sacco and Freni, in work recently published[16] and quoted by Malatesta, have made the three compounds $(CH_3NC)_2CoX_2$ (X = Cl, Br, NCS). The compound $(PhNC)_2CoBr_2$ has also been reported.[32] Magnetic measurements have been made on these four compounds and the magnetic moments we have calculated from the susceptibility data are given in column II of Table II. The compound $(C_2H_5NC)_2CoCl_2$ has been reported[33] but no magnetic data were given. We have prepared this compound as well as the corresponding bromide and determined their magnetic moments which are also given in column II of Table II. For the phenyl isonitrile compound the moment is compatible with either tetrahedral $(PhNC)_2CoBr_2$ molecules or an ionic structure containing the two tetrahedral ions $[(PhNC)_4Co]^{+2}$ and $[CoBr_4]^{-2}$.[1,2] In the first case the moment should be some kind of an average of the moments for $[(PhNC)_4Co]^{+2}$ and $[CoBr_4]^{-2}$ using the concept of an "average ligand field," but exactly what averaging process should be used is uncertain. If we make the simple assumption that an arithmetical average is appropriate, we then should conclude that the moment of the (unknown) tetrahedral cation $[(PhNC)_4Co)^{+2}$ must be about 4.26 B.M. This is not an unlikely number. If the substance has the ionic constitution the observed moment should be the root-mean-square of the moments of $[(PhNC)_4Co]^{+2}$ and $[CoBr_4]^{-2}$ whence we calculate a moment of about 4.20 B.M. for the $[Co(PhNC)_4]^{+2}$ ion which is also not unreasonable. Hence, the moment indicates that both of the two structural possibilities mentioned are possible but gives no basis for deciding between them.

For the remaining five compounds in Table II, however, the moments in column II lead to some definite and novel conclusions as to structure. According to Malatesta these compounds have magnetic susceptibilities which are averages between the values of the free Co^{+2} ion and of Co(II) in its inner complexes.[11] It therefore has been proposed that these compounds be formulated as $[Co(RNC)_4][CoX_4]$. While superficially this statement might appear reasonable, we shall now show that it is unacceptable quantitatively. The lowest possible moment we can assume for Co(II) in an "inner complex" is about 1.70 B.M. If we then assume that these substances contain $[Co(RNC)_4]^{+2}$ cations with moments of 1.70 B.M. and compute from this figure and the moments in column II the apparent moments of the $[CoX_4]^{-2}$ anions which they are supposed to contain we obtain the figures in column III. On comparison with the known moments of the $[CoX_4]^{-2}$ anions we see that these figures are all too low. Actually for planar, spin-

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TABLE II

MAGNETIC DATA FOR COMPLEXES OF THE TYPE $(RNC)_2CoX_2$

I		II	III	IV	V
R	X	μ(B.M.)[a b]	Apparent μ^b for CoX_4^{-2} with μ of $[Co(RNC)_4]^{+2}$ = 1.70 B.M.	Apparent μ^b for CoX_4^{-2} with diamagnetic $[Co_2(RNC)_8]^{+2}$	Literature value of μ for CoX_4^{-2} [c]
CH_3	Cl	3.26 (293)	4.29	4.61	4.76 ± 0.05[1]
CH_3	Br	3.31 (293)	4.36	4.68	4.79 ± .05[1]
CH_3	NCS	3.02 (293)	3.92	4.27	4.46 ± .04[2]
C_6H_5	Br	4.53 (293)	..	..	....
C_2H_5	Cl	3.33 (300)	4.39	4.74	4.76 ± .05[1]
C_2H_5	Br	3.41 (301)	4.52	4.82	4.79 ± .05[1]

[a] Temperature, °K., in parentheses; assuming the formula $(RNC)_2CoX_2$. [b] Diamagnetic corrections estimated by present authors. [c] The values are those which would be calculated from the susceptibilities at ~300°K. using the Curie law, since those in column IV are calculated from the Curie law (*i.e.*, taking θ to be zero); moments are corrected for diamagnetism.

paired $[(RNC)_4Co]^{+2}$ ions,[34] the correlations of Figgis and Nyholm would lead us to expect a moment considerably greater than 1.7 B.M. in which case the calculated apparent moments of the $[CoX_4]^{-2}$ ions would be still lower than the figures in column III. Hence we feel that the structure described for these compounds by Malatesta is unacceptable.

We wish to offer the hypothesis that these five compounds consist of diamagnetic $[Co(RNC)_4]_n^{2n+}$ cations (n must be even and perhaps most likely 2) and $[CoX_4]^{-2}$ anions. On this basis we calculate the apparent moments for the $[CoX_4]^{-2}$ anions given in column IV which compare rather satisfactorily with the authentic values given in column V. The result for $(CH_3NC)_2Co(NCS)_2$ is not really satisfactory but we reserve judgement until this and all of the compounds not measured by us have been checked. It would be premature to speculate upon the structure of the suggested $[(RNC)_4Co]_n^{2n+}$ ion, but experimental studies in progress may provide useful information.

Experimental

Preparation of Compounds. Bis-(*p*-toluidine)-Co(NCS)$_2$.—Absolute ethanol solutions of *p*-toluidine and anhydrous $Co(NCS)_2$ in stoichiometric proportions were mixed. A pink crystalline precipitate quickly formed and was washed with absolute ethanol and ether and dried in a desiccator.

Anal. Calcd. for $Co(C_7H_9N)_2(NCS)_2$: Co, 15.14; C, 49.35; H, 4.66; N, 14.39. Found: Co, 14.9; C, 48.97; H, 4.67; N, 14.68.

$(C_2H_5NC)_2CoCl_2$.—Prepared according to Hofmann and Bugge[33] by adding 3 g. of C_2H_5NC (obtained by the method of Jackson and McKusick[35]) to a solution of 3 g. of anhydrous $CoCl_2$ in 50 ml. of methanol. The volume of the solution was reduced by a pump until a microcrystalline green product precipitated. The solution was cooled in ice-salt and filtered. The product was washed with ether-methanol and dried *in vacuo* under continual pumping to remove excess isocyanide.

Anal. Calcd. for $Co(C_2H_5NC)_2Cl_2$: Co, 24.56; C, 30.03; H, 4.70; N, 11.67; Cl, 29.54. Found: Co, 24.5; C, 29.56; H, 4.47; N, 11.97; Cl, 29.17.

$(C_2H_5NC)_2CoBr_2$.—Prepared in the same manner as the chloride compound: 5.5 g. of anhydrous $CoBr_2$ dissolved in 50 ml. of methanol and 3 g. of C_2H_5NC added slowly with stirring. A fine olive-green precipitate separated. The solution was reduced in volume, cooled and filtered. The product was washed with alcohol and ether to remove a dark brown contaminant, blotted dry between filter papers and dried under continual pumping.

Anal. Calcd. for $Co(C_2H_5NC)_2Br_2$: Co, 17.92; C, 21.91; H, 3.06; N, 8.52; Br, 48.59. Found: Co, 17.9; C, 21.67; H, 3.27; N, 8.63; Br, 48.30.

Magnetic Measurements.—Measurements were made by the Gouy method as previously described.[1,2] The molar diamagnetic correction for ethyl isocyanide was taken to be -34×10^{-6}.

Acknowledgment.—We are grateful to the National Science Foundation for financial support.

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(34) It has been pointed out[1,2] that tetrahedral Co(II) complexes cannot be spin-paired unless the field is so strong as to change the electronic configuration from d^7 to d^6s or d^6p which seems improbable and is, at any rate, so far without precedent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS]

Sulfoxides as Ligands. I. A Preliminary Survey of Methyl Sulfoxide Complexes

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The preparation of a large number of complexes of dimethyl sulfoxide is reported. The structures of some of them have been elucidated on the basis of infrared and visible spectra, magnetic measurements and steric considerations. It appears that oxygen is the donor atom in all cases reported except toward Pd(II) in $[(CH_3)_2SO]_2PdCl_2$ where infrared evidence suggests Pd←S bonding. Some of the complexes, such as $[(CH_3)_2SO]_2SnCl_4$ and $[(CH_3)_2SO]_2FeCl_3$, have great thermal stability. $NiCl_2 \cdot 3[(CH_3)_2SO]$, $CoCl_2 \cdot 3[(CH_3)_2SO]$ and $CoBr_2 \cdot 3[(CH_3)_2SO]$ are shown to contain, respectively, the tetrahedral anions $NiCl_4^{-2}$, $CoCl_4^{-2}$ and $CoBr_4^{-2}$.

Several years ago we commenced an investigation of the ability of the sulfur-oxygen grouping in sulfoxides (RR'SO) to function as an electron donor. Positive results soon were obtained and several preliminary reports have been made.[1] Recent attention in trade literature to the commercial availability and unusually favorable solvent properties of dimethyl sulfoxide (DMSO) has prompted us to issue a preliminary survey of the complexes we have prepared with this sulfoxide. Most of them have been or are being investigated in more detail, especially in respect to their spectral and magnetic properties and the light such properties shed upon the structures of

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(1) F. A. Cotton, Annual Reports of USAEC Contract AT(30-1)-1965, No. NYO-8653 for period 9/15/57-9/14/58 and No. NYO-2246 for period 9/15/58-9/14/59.