

# THE MAGNETIC PROPERTIES OF $\mu\mu'$ -DIHYDROXO-TETRAKISETHYLENEDIAMINE DICHRONIUM (III) SALTS AT HELIUM TEMPERATURES

BY B. JASIEWICZ, M. F. RUDOLF AND B. JEŻOWSKA-TRZEBIATOWSKA

Institute of Chemistry, University of Wrocław\*

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The results of magnetic studies of the dimeric  $\mu\mu'$ -Dihydroxo-Tetrakisethylenediamine Dichromium (III) salts in the temperature range 1.6°–300°K are presented. The observed magnetic coupling of pairs of  $\text{Cr}^{3+}$  ions is interpreted in terms of the Van Vleck — Heisenberg — Dirac model of antiferromagnetism. On the basis of magnetic and IR-spectral studies the occurrence of the superexchange coupling of  $\text{Cr}^{3+}$  ions in the  $\text{Cr} \begin{array}{c} \text{OH} \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \text{Cr}$  nucleus is demonstrated.

## 1. Introduction

Polynuclear coordination compounds of  $d$ -electronic elements are interesting objects for studying spin-spin interactions. The synthesis of the appropriate compounds enables the study to be made of both the mechanism and the nature of the magnetic interactions for the  $d^n-d^n$ ,  $d^n-d^n-d^n \dots (d^n)_k$  electronic configurations as well as for the mixed configurations of the  $d^n-d^m$  type. Not only the number of interacting paramagnetic centers but also their spatial arrangements are well defined for such magnetically concentrated systems. Therefore, it is possible to verify experimentally the well-known models of antiferro- and ferromagnetic interactions of paramagnetic ions with regard to the intramolecular antiferro- and ferromagnetism [1–6].

In this paper the results of magnetic susceptibility studies of  $\mu\mu'$ -dihydroxo-tetrakisethylenediamine dichromium (III) salts  $[\text{Cr}_2(\text{OH})_2 \text{en}_4]\text{X}_4$  where  $\text{X} = \text{Cl}, \text{Br}, \text{J}$  in the temperature range 1.6°–300°K are presented.

The two chromium (III) atoms are bounded in the  $\mu\mu'$ -dihydroxo-tetrakisethylenediamine dichromium (III) ion by a double hydroxo-bridge. The remaining coordination positions are occupied by the  $\sigma$ -donating nitrogen atoms of the ethylenediamine molecules.

\* Address: Instytut Chemii, Uniwersytet Wrocławski, Joliot-Curie 14, 50-383 Wrocław, Poland.

The symmetry of the molecule is  $D_{2h}$  taking into account only the ligand donor atoms. The local symmetry of the chromium atoms is  $C_{2v}$ . A similar structure was reported for a series of  $\mu\mu'$ -dihydroxo-octaamino-dicobalt (III)  $[\text{Co}_2(\text{OH})_2(\text{NH}_3)_8]^{4+}$  complexes [7, 8].

Till now, the thermomagnetic properties of the following chromium (III) clusters have been studied (Table I).

TABLE I

Electron System	Compound	Ref.
$d^3-d^3$	$[(\text{NH}_3)_5 \text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5]^{5+}$	[2, 9, 10]
	$[(\text{NH}_3)_5 \text{Cr}-\text{OH}-\text{Cr}(\text{OH})(\text{NH}_3)_4]^{4+}$	[2, 9, 10]
	$[(\text{NH}_3)_5 \text{Cr}-\text{OH}-\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_4]^{5+}$	[2, 9, 10]
	$[(\text{NH}_3)_5 \text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]^{4+}$	[2, 9, 10]
	$[(\text{H}_2\text{O})_4 \text{Cr}-(\text{OH})_2-\text{Cr}(\text{H}_2\text{O})_4](\text{VO}_3)_4$	[11]
$d^3-d^3-d^3$	$[\text{Cr}-\text{O}-\text{Cr}](\text{VO}_3)_4$	[11]
	$[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6]\text{Cl} \cdot 8 \text{H}_2\text{O}$	[12, 13]
	$[\text{Cr}_3\text{O}(\text{CH}_2\text{ClCOO})_6]\text{Cl} \cdot 9 \text{H}_2\text{O}$	[13]
	$[\text{Cr}_3\text{O}(\text{CH}_2\text{ClCOO})_6]\text{CH}_2\text{ClCOO} \cdot 4 \text{H}_2\text{O}$	[14]
	$[\text{Cr}_3\text{O}(\text{HCOO})_6]\text{HCOO}$	[14]
$d^3-d^3-d^3-d^3$	$[\text{Cr}_3\text{O}(\text{C}_2\text{H}_5\text{COO})_6]\text{NO}_3 \cdot 3 \text{H}_2\text{O}$	[14]
	$[\text{Cr}_4(\text{OH})_6 \text{en}_6]\text{J}_6$	[15]
	$[\text{Cr}_4(\text{OH})_6 \text{en}_6](\text{N}_3)_6$	[16, 17]
	$[\text{Cr}_4(\text{OH})_6 \text{en}_6](\text{SO}_4)_3$	[18]

As far as dimeric chromium (III) clusters are concerned, only the room temperature magnetic moments of a few chromium (III) dimers were determined besides those of the above-listed species.

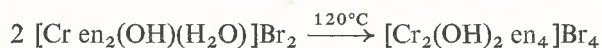
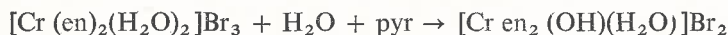
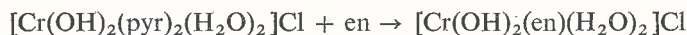
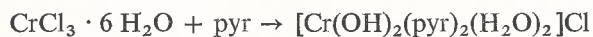
Unfortunately, no conclusions about the type and magnitude of the Cr-Cr spin-spin interactions in those compounds may be drawn from the figures given in Table II.

TABLE II

Compound	$\mu_{\text{eff}}$ [BM]
$[\text{Cr}_2(\text{OH})_2(\text{en})_4](\text{S}_2\text{O}_6)_2$	3.81
$[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{Br}_4 \cdot 2 \text{H}_2\text{O}$	3.55
$\text{K}_4[\text{Cr}_2(\text{OH})_2(\text{ox})_4] \cdot 6 \text{H}_2\text{O}$	3.63
$\text{Na}_4[\text{Cr}_2(\text{OH})_2(\text{ox})_4] \cdot 4 \text{H}_2\text{O}$	3.43
$[\text{Cr}_2(\text{OH})_2(\text{ox})_2(\text{en})_2]$	3.53
$[\text{Cr}_2(\text{OH})_2(\text{gly})_4] \cdot \text{H}_2\text{O}$	3.37
$[\text{Cr}_2(\text{OH})_2(\text{ala})_4] \cdot \text{H}_2\text{O}$	3.43
$[\text{Cr}(\text{en})_3][\text{Cr}(\text{ox})_3]$	3.55
$[\text{Cr}(\text{ox})(\text{en})_2][\text{Cr}(\text{ox})_2(\text{en})]$	3.74
$[\text{Cr}(\text{OH})(\text{H}_2\text{O})(\text{en})_2][\text{Cr}(\text{OH})(\text{H}_2\text{O})(\text{ox})_2]$	3.88

## 2. Experimental part

The chlorides, bromides and iodides of  $\mu\mu'$ -dihydroxo-tetrakisethylenediamine dichromium (III) were synthesized according to the following reaction scheme given by Pfeiffer [20]:



where: pyr = pyridine, en = ethylenediamine

TABLE III

Magnetic properties of the  $\mu\mu'$ -Dihydroxo-Tetrakisethylenediamine Dichromium (III) Chloride  
 $[\text{Cr}_2(\text{OH})_2 \text{en}_4]\text{Cl}_4 \cdot 4 \text{H}_2\text{O}^1$

$T$ °K	$\chi_M \cdot 10^3$	$\mu^2_{\text{eff}}$ [BM]	$T$ °K	$\chi_M \cdot 10^3$	$\mu^2_{\text{eff}}$ [BM]
1.8	0.121	0.00	40.0	26.180	8.45
2.6	0.235	0.00	45.0	25.980	9.43
3.2	0.708	0.02	50.0	25.158	10.15
4.2	0.963	0.03	55.0	25.317	11.23
5.0	1.520	0.06	60.0	25.102	12.15
6.0	1.418	0.07	65.0	25.312	13.27
7.0	2.740	0.15	70.0	24.643	13.91
8.0	5.363	0.35	75.0	24.400	14.76
9.0	7.537	0.55	80.0	24.018	15.50
10.0	10.224	0.83	85.0	23.147	15.87
12.0	11.957	1.16	90.0	23.511	17.07
14.0	15.178	1.71	95.0	23.020	17.64
16.0	18.719	2.42	100.0	23.003	18.55
18.0	20.504	2.98	114.5	21.567	19.92
20.0	20.805	3.36	129.0	19.433	20.22
22.0	20.753	3.68	143.3	18.508	21.39
24.0	22.640	4.38	178.0	16.930	24.31
26.0	22.917	4.81	185.0	16.024	23.91
28.0	23.280	5.26	200.0	14.125	22.79
30.0	24.071	5.82	210.0	13.280	22.49
32.0	24.673	6.37	231.0	13.216	24.62
34.0	24.582	6.74	250.5	12.807	25.48
36.0	25.345	7.36	273.0	11.807	26.00
38.0	25.630	7.86	285.0	11.133	25.60
			298.5	10.577	25.47

<sup>1</sup> the molar susceptibility was calculated for the whole molecule (per 2 chromium atoms).

TABLE IV

Magnetic properties of the  $\mu\mu'$ -Dihydroxo-Tetrakisethylenediamine Dichromium (III) Bromide  
 $[\text{Cr}_2(\text{OH})_2 \text{en}_4]\text{Br}_4 \cdot 2.5 \text{H}_2\text{O}^1$

$T$ °K	$\chi_M \cdot 10^3$	$\mu^2_{\text{eff}}$ [BM]	$T$ °K	$\chi_M \cdot 10^3$	$\mu^2_{\text{eff}}$ [BM]
2.0	2.120	0.03	50.0	43.821	17.67
3.0	3.971	0.10	55.0	44.078	19.55
4.0	8.513	0.28	60.0	41.502	20.08
5.0	16.903	0.68	65.0	40.079	21.01
6.0	22.867	1.11	70.0	38.640	21.82
7.0	31.062	1.75	75.0	36.711	22.21
8.0	40.120	2.59	80.0	34.073	21.99
9.0	41.227	2.99	90.0	31.900	23.15
10.0	42.597	3.44	95.0	30.402	23.29
12.0	46.753	4.53	100.0	30.257	24.40
14.0	49.284	5.57	114.0	27.851	25.61
16.0	51.530	6.65	129.0	23.843	24.81
18.0	52.539	7.63	141.3	22.716	25.89
20.0	53.619	8.65	162.0	18.124	23.68
22.0	54.804	9.73	174.5	19.268	27.12
24.0	55.034	10.65	187.0	18.076	27.26
26.0	54.071	11.34	201.0	16.453	26.67
28.0	53.672	12.12	216.5	16.300	28.46
30.0	53.080	12.84	232.0	15.980	29.90
32.0	53.104	13.71	247.0	15.033	29.95
34.0	50.978	13.98	267.0	13.482	29.03
38.0	49.920	15.30	285.0	12.888	29.63
40.0	48.617	15.69	298.0	12.048	28.96
45.0	46.203	16.77			

<sup>1</sup> the molar susceptibility was calculated for the whole molecule (per 2 chromium atoms).

The magnetic susceptibility measurements in the temperature range 1.6°–300°K and at the magnetic field strength of 6.3 KOe were carried out using the Faraday method. The temperature dependences of the molar susceptibilities (calculated per molecule) and of  $\mu^2_{\text{eff}}$  are given Tables III–V and shown on Figs 1–3.

The infrared spectra of the investigated complexes in Nujol and hexachlorobutadiene suspensions, as well in KBr pellets were obtained with a Perkin-Elmer spectrophotometer Model 621 and with a Carl-Zeiss Jena spectrophotometer Model UR-20. The theoretical magnetic susceptibility curves were calculated with an Odra 1204 computer.

### 3. Results and discussion

Using the Lewis formula [2] for the temperature dependence of the magnetic susceptibility of the  $d^3$ – $d^3$  coupled system:

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \frac{3 \exp(-2J/kT) + 30 \exp(-6J/kT) + 84 \exp(-12J/kT)}{1 + 3 \exp(-2J/kT) + 5 \exp(-6J/kT) + 7 \exp(-12J/kT)}$$

TABLE V

Magnetic properties of the  $\mu\mu'$ -Dihydroxo-tetrakisethylenediamine Dichromium (III) Iodide  
 $[\text{Cr}_2(\text{OH})_2 \text{en}_4]\text{I}_4^1$

$T^\circ\text{K}$	$\chi_M \cdot 10^2$	$\mu_{\text{eff}}^2$ [BM]	$T^\circ\text{K}$	$\chi_M \cdot 10^2$	$\mu_{\text{eff}}^2$ [BM]
2.0	3.420	0.55	50.0	6.297	25.40
3.0	6.483	1.57	55.0	5.628	24.97
4.0	10.730	3.46	60.0	5.200	25.17
5.0	18.802	7.58	65.0	4.717	24.73
6.0	12.635	6.12	75.0	4.433	26.82
7.0	13.023	7.35	80.0	4.301	27.75
8.0	12.954	8.36	85.0	3.848	26.38
9.0	13.281	9.64	90.0	3.820	27.73
10.0	13.054	10.53	95.0	3.698	28.34
12.0	13.011	12.59	100.0	3.316	26.75
14.0	12.975	14.65	110.0	2.977	26.41
16.0	12.467	16.09	123.0	2.926	29.03
18.0	11.300	16.41	136.0	2.640	28.96
20.0	11.002	17.75	150.0	2.130	25.77
22.0	10.908	19.36	162.0	2.081	27.19
24.0	10.384	20.10	178.0	2.119	30.42
26.0	9.617	20.17	191.0	1.977	30.46
28.0	9.403	21.24	207.0	1.842	30.75
30.0	9.018	21.82	222.0	1.790	32.05
32.0	8.401	21.68	234.0	1.683	31.76
34.0	8.270	22.68	248.0	1.534	30.68
36.0	8.017	23.28	265.0	1.423	30.42
38.0	7.527	23.07	280.0	1.328	29.99
40.0	7.409	23.90	295.0	1.282	30.50

<sup>1</sup> the molar susceptibility was calculated for the whole molecule (per 2 chromium atoms).

The values of the exchange integrals  $-J$  were calculated by fitting the experimental data into the above equation. These results are shown in Table VI.

From these results one may conclude that the exchange integrals depend on the kind of anions in the outer coordination sphere, decreasing in the following sequence:  $-J_{\text{Cl}} > -J_{\text{Br}} > -J_{\text{I}}$ . The dependence of the exchange integrals on the nature of the outer-sphere anions may be due to three effects:

1. the covalent radii of the anions determining the magnetic isolation of the neighbouring Cr-Cr pairs in the crystal lattice. Therefore, the effective coupling of the  $\text{Cr}^{3+}$  ions should be interpreted in this case in terms of four interacting paramagnetic ions arranged rhombically;

2. the contribution of the outer-sphere anions to the super-exchange interactions shown schematically below:



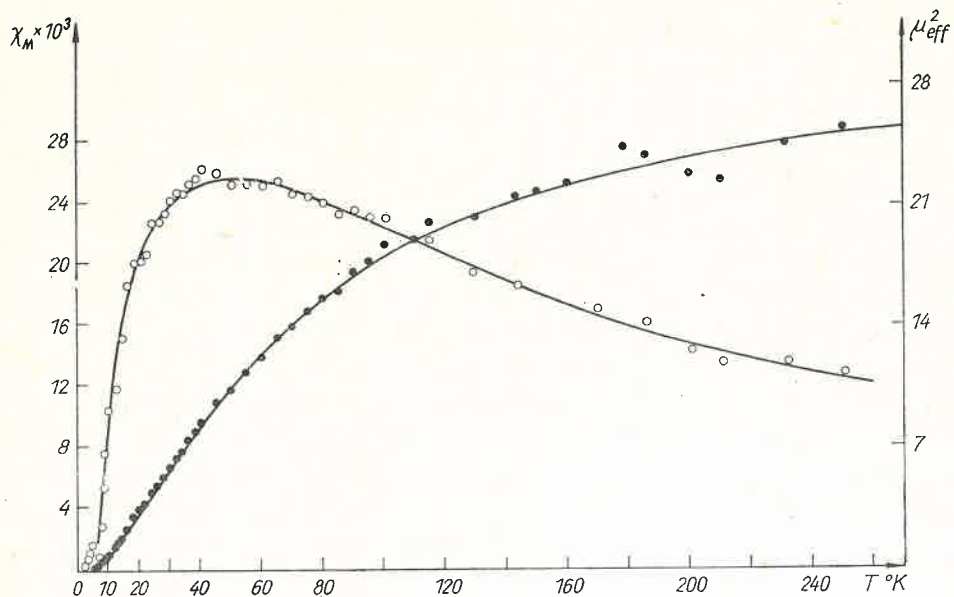


Fig. 1. Dependence of molar magnetic susceptibility (○) and  $\mu_{\text{eff}}^2$  (●) on temperature for  $[\text{Cr}_2(\text{OH})_2 \text{en}_4]\text{Cl} \cdot 4 \text{H}_2\text{O}$ . Theoretical curves given by solid lines

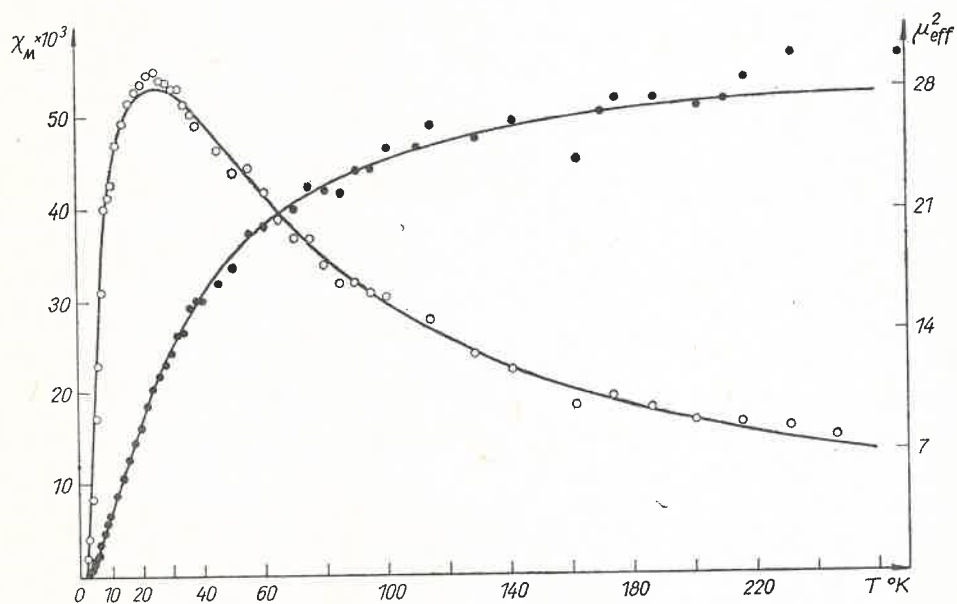


Fig. 2. Dependences of molar magnetic susceptibility (○) and  $\mu_{\text{eff}}^2$  (●) on temperature for  $[\text{Cr}_2(\text{OH})_2 \text{en}_4]\text{Br}_4 \cdot 2.5 \text{H}_2\text{O}$ . Theoretical curves given by solid lines

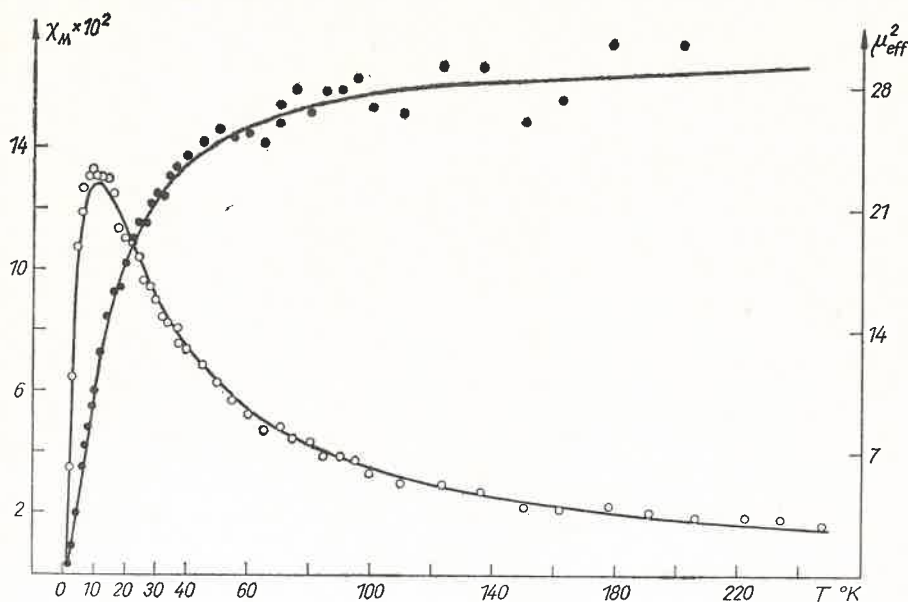


Fig. 3. Dependences of molar magnetic susceptibility (○) and  $\mu_{\text{eff}}^2$  (●) on temperature for  $[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{J}_4$ . Theoretical curves given by solid lines

3. the variation of the chromium-chromium distance within the pair of interacting ions due to the changes of the valence angles in the  $\text{Cr}(\text{OH})_2$  Cr core.

In order to find out, which one of the above given mechanisms determines the magnetic properties of the investigated dimers, the IR spectra were obtained.

TABLE VI  
Values of the exchange integrals  $-J$  for investigated  $\mu\mu'$ -Dihydroxo-Tetrakisethylene-diamine Dichromium (III) salts

Compound	$-J$ [ $\text{cm}^{-1}$ ]
$[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{Cl}_4 \cdot 4 \text{H}_2\text{O}$	23.5
$[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{Br}_4 \cdot 2.5 \text{H}_2\text{O}$	11.3
$[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{J}_4$	4.7

TABLE VII  
Characteristic frequencies of the  $\text{Cr}_2(\text{OH})_2$  nucleus in Dimeric  $\mu\mu'$ -Dihydroxodichromates (III)<sup>1</sup>

Compound	$\nu_{B_{1u}}$	$\nu_{B_{2u}}$
$[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{Cl}_4 \cdot 4 \text{H}_2\text{O}$	515	761
$[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{Br}_4 \cdot 2.5 \text{H}_2\text{O}$	530	751
$[\text{Cr}_2(\text{OH})_2(\text{en})_4]\text{J}_4$	541	723

<sup>1</sup> the frequencies are given in  $\text{cm}^{-1}$ .

Double-bridged dimeric cores exhibit two characteristic absorption bands due to the stretching modes which are coupled with the deformation modes of the four-membered Me  $\begin{array}{c} \diagup \text{X} \\ \diagdown \text{X} \end{array}$  Me ring. This was proved for the cores of dimeric  $\mu\mu'$ -dihydroxodicobaltates (III) [21],  $\mu\mu'$ -dioxo-oxodimolybdates (V) [22-24], arsenates (V) and osmates (VI) [25].

The observed characteristic frequencies of the  $\text{Cr}(\text{OH})_2$  Cr core, having  $B_{1u}$  and  $B_{2u}$  symmetries are presented in Table VII. As indicated by the figures given in Table VII, a considerable increase of the  $B_{1u}$  frequency and decrease of the  $B_{2u}$  frequency are observed in the following sequence of anions: Cl, Br, J. This phenomenon is due to the changes of the valence angles in the Me  $\begin{array}{c} \diagup \text{OH} \\ \diagdown \text{OH} \end{array}$  Me core, as has been shown by Wing [24] and Rudolf [23]. The Cr-OH-Cr valence angles in the studied Cr (III) dimers decrease in the following sequence of outer-sphere anions: Cl > Br > J. Therefore a slight decrease of the Cr-Cr distance in the  $\mu\mu'$ -dihydroxo-tetrakisethylenediamine dichromium (III) iodide in comparison with those in the analogous chloride and bromide salts should be observed.

If the direct metal-metal interactions were the most effective ones, the  $-J$  values would change in a sequence reverse to that shown in Table VI. The significant increase of the direct metal-metal exchange integrals with the diminution of the distance between the coupled  $\text{Cr}^{3+}$  ions indicates that a superexchange between those ions takes place through the bridging oxygen atoms.

Kanamori has calculated the theoretical dependence of the exchange integral  $-J$  on the valence angle of the Me-O-Me systems [26].

In the case of superexchange interactions the decrease of the valence angle should lead to a decrease of the exchange integral  $-J$ . In extreme cases also a change of the sign of the exchange integral may be observed at angles close to  $90^\circ$ , which corresponds to the antiferromagnetic — ferromagnetic superexchange transition.

Our results presented in this paper confirm the theoretical results reported by Kanamori and are in excellent agreement with them. It has been proved that the dominating effect determining the magnetic properties of the studied chromium (III) dimers is the superexchange interaction of the paramagnetic  $\text{Cr}^{3+}$  ions through the bridging oxygen atoms.

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