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Structure, Spectroscopy and Magnetism of Di-iodo-bridged Tetrahedral Cobalt(II) Compounds. The Crystal and Molecular Structures of Di-μ-iodo-bis[iodotriphenylphosphinecobalt(II)] bis(benzene) and Di-μ-iodo-bis[iodotriphenylphosphineoxidecobalt(II)] bis(benzene)

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Abstract

The crystal and molecular structures of two dinuclear Co(II) compounds of formula $[Co_2I_4(L)_2] \cdot (C_6H_6)_n$ ($L = PPh_3$ or $OPPh_3$; $n = 1, 2$) are described.

Compound (**a**) with L = PPh_3 crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.769(4)$, $b = 12.447(4)$ and $c = 9.338(6)$ Å, $\alpha = 113.82(4)$, $\beta = 94.21(4)$, $\gamma = 110.20(2)°$; $Z = 1$. Compound (**b**) with L = $OPPh_3$ crystallizes in the monoclinic space group $C2/c$ with $a = 23.649(4)$, $b = 9.984(3)$, $c = 22.153(4)$ Å, $\beta = 109.92(2)°$; $Z = 4$. The structures of both compounds are very similar and consist of centrosymmetric dinuclear Co_2I_2 units, with Co–I distances of 2.614 and 2.623 Å in (**a**); 2.648 and 2.653 Å in (**b**) and Co–I–Co angles of 78.8° (**a**), 79.3° (**b**). The tetrahedral coordination around Co is completed by an iodide ion (distances of 2.52 Å (**a**) and 2.53 Å (**b**)) and a ligand donor atom (Co–P in (**a**) = 2.36 Å and Co–O in (**b**) = 1.917 Å). The dimeric Co_2I_2 has a planar geometry which appears to be solely determined by the size of iodide ions, with Co···Co distances of 3.32 Å in (**a**) and 3.38 Å in (**b**) and I···I bridge distances 4.05 Å (**a**) and 4.08 Å (**b**). These I–I contacts are about equal to twice the van der Waals radius of iodide ions. The benzenes are present as lattice molecules. Ligand-field and far-IR spectra are consistent with the tetrahedral geometry for cobalt(II).

The magnetic exchange between the cobalt(II) ions appears to be strongly antiferromagnetic, as deduced from magnetic susceptibility studies at temperatures down to 4 K. Fitting with a Heisenberg $S = ½$ dimer results in J values of −33 K (**a**) and −35 K (**b**), with g values of 2.45 (**a**) and 2.95 (**b**).

Introduction

During the last decade a variety of transition-metal compounds of a dimeric nature have been reported and studied in detail with respect to structure and magnetic exchange coupling [1, 2].

Among the metal ions, both Cu(II) and Cr(III) have been studied in great detail, especially with OH-ligands bridging the metal ions [2, 3]. In these cases even quantitative relationships have been developed to correlate the structure with the magnitude of the exchange interaction. For other metal ions and other bridging ligands, fewer studies have been undertaken. A number of chloride- and fluoride-bridged systems are known with first-row transition metal ions [4, 5], also some dimers have been reported with bromide as bridging ligand [6]. An interesting situation arises with iodide as a bridging ligand: the van der Waals radius of the iodide prevents the metal ions coming close together (for octahedral coordination of Co or Ni the closest contact may be about 4.0 Å, whereas for tetrahedral coordination the closest contact may be about 3.4 Å [7].)

Unfortunately, the number of dimeric systems having the M_2I_2 bridging unit is rather small, and only very few magnetic studies have been reported so far [8]. Our earlier work [9] has resulted in the compounds CoI_2L with L = PPh_3 and $OPPh_3$, for which the spectral data suggested tetrahedral Co(II) and magnetic measurements indicated a strong magnetic interaction of antiferromagnetic nature.

To determine the structure of these compounds (bridging ligands or bridging iodide) and to correlate the structure with the magnetic behaviour, the crystal structures of both compounds were determined.

Experimental

Synthesis

Reagent grade triphenylphosphine (Fluka) and triphenylphosphineoxide (Aldrich) were purified by recrystallization followed by sublimation. Anhydrous

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TABLE I. Crystallographic Data. Compound (a): Di-μ-iodo-bis(iodotriphenylphosphinecobalt(II))bis(benzene). Compound (b): Di-μ-iodo-bis(iodotriphenylphosphineoxidecobalt(II))bis(benzene).

	Compound (a)	Compound (b)
Formula	$Co_2I_4P_2C_{48}H_{42}$	$Co_2I_4O_2P_2C_{48}H_{42}$
Molecular weight	1306.30	1338.30
a (Å)	12.769(4)	23.649(4)
b (Å)	12.447(4)	9.984(3)
c (Å)	9.338(6)	22.153(4)
α (°)	113.82(4)	
β (°)	94.21(4)	109.92(2)
γ (°)	110.20(2)	
V (Å^3)	1237.49	4917.34
Temperature	293 K	183 K
Space group	$P-1$	$C2/c$
Molecules/Cell	$Z = 1$	$Z = 4$
Calculated density	1.75 g cm^{-3}	1.81 g cm^{-3}
Radiation	Mo K_α, graphite monochromatized	
Absorption coefficient	32.3 cm^{-1}	32.6 cm^{-1}
Crystal size (mm)	0.55 × 0.2 × 0.1	0.5 × 0.2 × 0.4
Transmission- min.	0.48	0.41
factors max.	0.70	0.76
$\omega/2\theta$ scan-range	$2° < \theta° < 27.5°$	$2° < \theta° < 30°$
Reflections measured	6309	11839 (indep. 5962)
Reflections used	4404	4300
Discrimination	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R	0.023	0.033
R_w	0.033	0.040
$w = 1/\sigma^2(F)$ see Ref. 10		

cobalt iodide (Ventron) was washed with benzene in order to eliminate excess iodine.

Dry cobalt iodide in excess (0.05 mol) and 0.01 mol of ligand were refluxed for two h in 100 ml of anhydrous, oxygen-free benzene. After hot filtration in order to eliminate the excess of cobalt iodide, crystallization occurred by slow cooling of the solution.

The triphenylphosphineoxide complex yielded green prismatic crystals and also green needles, differing in the number of benzene molecules. The latter crystals (designated **b**), which were very air-sensitive and which contained two benzene molecules, were used for the collection of crystallographic data. The former crystals (designated **b'**), with one benzene molecule and which were less air-sensitive, were used for magnetic measurements and recording electronic and infra-red spectra. Analytical details of both compounds were published previously [9]. The parity of both compounds was checked by elemental analysis.

Spectroscopy

Far-infrared spectra were recorded on a Beckman model FIR 720 as polyethylene pellets. Reflectance spectra were recorded on a Beckman model 5240 spectrophotometer.

Magnetism

Magnetic susceptibility measurements between 80 K and 300 K were carried out on a Faraday balance, and between 4 and 80 K on a parallel-field vibrating sample magnetometer PAR model 150 A equipped with a Janis cryostat. Calibrations were made using $CoHg(SCN)_4$.

Collection of X-ray Data, Structure Solution and Refinement

The crystals of the two compounds were sealed in Lindemann capillaries to prevent decomposition caused by moisture sensitivity of the purple-red (a) and dark green (b) compounds.

Determination of lattice parameters and data collection were carried out with an ENRAF NONIUS CAD-4 diffractometer, as previously described [10]. Corrections were taken for Lorentz and polarization effects, also both datasets are corrected for absorption. Crystallographic data are summarized in Table I.

Both structures were solved by Patterson maps determining Co and I positions, followed by Fourier synthesis revealing all non-hydrogen atoms of the ligands and benzene solvent molecules. Refinement was carried out using full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogens were placed

TABLE II. Compound (a): di-μ-bis(iodotriphenylphosphinecobalt(II))bis(benzene). Fractional Atomic Coordinates (Co, I × 10^5; P, C × 10^4). Isotropic Thermal Parameters (Co, I, P × 10^3; C × 100 or 10) (estimated standard deviations in the least significant digits are given in parentheses).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(Iso)
Co	9239(3)	–4886(3)	6057(4)	3236(10)
I(1)	–11296(2)	–7904(2)	10767(2)	4030(4)
I(2)	11515(2)	–25543(2)	–8569(3)	5492(10)
P	2314(1)	850(1)	3106(1)	3242(12)
C(11)	2519(2)	–16(3)	4191(3)	368(7)
C(12)	3586(3)	289(4)	5079(5)	517(11)
C(13)	3671(4)	–374(5)	5967(6)	666(14)
C(14)	2726(4)	–1305(4)	5936(5)	624(14)
C(15)	1662(4)	–1637(4)	5035(6)	618(14)
C(16)	1563(3)	–989(4)	4158(5)	505(10)
C(21)	1997(2)	2127(3)	4550(3)	350(7)
C(22)	1589(3)	2822(3)	4009(4)	464(9)
C(23)	1360(3)	3823(3)	5062(5)	544(11)
C(24)	1529(3)	4117(3)	6685(5)	579(11)
C(25)	1923(4)	3419(4)	7223(4)	629(13)
C(26)	2162(3)	2436(4)	6165(4)	529(11)
C(31)	3706(2)	1669(3)	2829(3)	357(7)
C(32)	3990(3)	1059(3)	1407(4)	475(9)
C(33)	5037(3)	1682(4)	1133(5)	576(11)
C(34)	5779(3)	2874(4)	2255(5)	528(11)
C(35)	5519(3)	3474(4)	3668(5)	569(11)
C(36)	4477(3)	2881(3)	3946(4)	484(9)
C(41)	3497(7)	–3217(5)	1644(7)	88(2)
C(42)	2512(6)	–4022(6)	1746(6)	83(2)
C(43)	2469(5)	–5130(5)	1803(6)	76(2)
C(44)	3408(5)	–5388(5)	1766(6)	76(2)
C(45)	4399(5)	–4572(5)	1678(6)	75(2)
C(46)	4443(5)	–3501(6)	1595(6)	85(2)

at distances of 96 pm from the parent atoms. Only isotropic thermal parameters of the hydrogen atoms were refined.

Final difference Fourier synthesis showed no significant deviations above background for compound (**b**). The non-bridging iodine of the phosphine complex (**a**) revealed a degree of disorder about 0.023 in a distance of 42 pm. For refinement this peak is ignored, because disorder of other atoms was not observed.

Fractional coordinates and isotropic temperature parameters are listed in Tables II and III for both compounds. Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the Editor.

All calculations were carried out with the Leiden University Amdahl V7B computer. The principle programs used have been described previously [10].

TABLE III. Compound (b): di-μ-bis(iodotriphenylphosphineoxidecobalt(II))bis(benzene). Fractional atomic coordinates (Co, I × 10^5; P, O, C × 10^4). Isotropic thermal parameters (Co, I × 10^3; O, P, C × 100 or 10) (e.s.d.s in the least significant digits are given in parentheses).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(Iso)
Co	7488(3)	47877(6)	3655(3)	2785(15)
I(1)	418(1)	67400(3)	4960(2)	3040(9)
I(2)	16349(2)	55225(4)	575(2)	4197(11)
O	965(2)	3872(3)	1173(2)	361(10)
P	1039(1)	2431(1)	1412(1)	294(3)
C(11)	351(2)	1851(5)	1494(2)	325(13)
C(12)	–109(3)	2756(6)	1400(3)	42(2)
C(13)	–635(3)	2324(8)	1481(3)	53(2)
C(14)	–710(3)	1043(9)	1639(3)	55(2)
C(15)	–263(3)	131(7)	1721(3)	52(2)
C(16)	286(3)	517(5)	1655(3)	41(2)
C(21)	1609(2)	2453(5)	2189(2)	367(14)
C(22)	1675(3)	3598(6)	2551(3)	45(2)
C(23)	2084(3)	3665(7)	3165(3)	53(2)
C(24)	2455(3)	2591(8)	3411(3)	57(2)
C(25)	2402(4)	1444(7)	3056(3)	63(2)[a]
C(26)	1983(3)	1365(6)	2440(3)	53(2)[a]
C(31)	1264(2)	1335(5)	901(2)	314(12)
C(32)	910(3)	326(5)	536(3)	382(15)
C(33)	1112(3)	–433(5)	123(3)	45(2)
C(34)	1654(3)	–174(6)	69(3)	42(2)
C(35)	2010(3)	847(6)	422(3)	44(2)
C(36)	1819(2)	1590(5)	834(3)	402(15)
C(41)	3320(4)	2999(7)	2141(5)	61(2)
C(42)	3742(4)	2299(9)	2591(4)	65(2)
C(43)	4142(4)	1599(9)	2407(6)	85(3)[a]
C(44)	4119(4)	1581(8)	1776(6)	83(4)[a]
C(45)	3687(4)	2327(9)	1341(4)	65(3)
C(46)	3285(3)	3034(7)	1521(4)	60(2)

[a] These atoms show high thermal anisotropy.

Results and Discussion

Molecular and Crystal Structures of Compounds (a) and (b)

The bond lengths and angles are listed in Tables IV and V and the molecular structures and labelling of the atoms are shown in Figs. 1, 2. Both molecular structures are very similar with a crystallographic center of symmetry, and differ only in type of donor atom of the ligand. The dinuclear coordination compounds consists of two identical tetrahedral-like CoI_2L units (L = PPh_3 or $OPPh_3$) connected along a common iodide–iodide edge such that the two cobalt and two bridging iodide ions form a strictly planar rhombus. The Co_2I_2 fragments have only slight differences in bond length and angles. The I–I distances (4.05 (**a**) and 4.08 Å (**b**)) are about equal to twice the van der Waals radius of the iodides. This is also described for the comparable $(Fe(NO)_2I)_2$

TABLE IV. Bond Distances and Other Significant Interatomic Distances (Å) and Angles for Compound (a) (e.s.d.s in the least significant digits in parentheses).

Co–I(1)	2.6138(4)	I(1)–Co–I(1)[a]	101.23(1)
Co–I(1)[a]	2.6230(4)	Co–I(1)–Co[a]	78.77(1)
Co–I(2)	2.5150(4)	I(1)–Co–I(2)	114.35(2)
Co–P	2.3635(8)	I(1)–Co–P	109.50(2)
Co–Co[a]	3.3230(7)	I(2)–Co–I(1)[a]	112.39(2)
I(1)–I(1)[a]	4.0474(4)	I(2)–Co–P	110.54(2)
I(1)–I(2)	4.3101(3)	P–Co–I(1)[a]	108.36(2)
I(1)–I(1)[a]	4.2697(3)	Co–P–C(11)	113.25(10)
I(1)–P	4.0672(7)	Co–P–C(21)	115.17(9)
I(2)–P	4.0102(7)	Co–P–C(31)	111.09(10)
P–I(1)a	4.0463(8)		
P–C(11)	1.817(3)	C(11)–P–C(21)	104.31(13)
P–C(21)	1.820(3)	C(11)–P–C(31)	107.47(13)
P–C(31)	1.816(3)	C(21)–P–C(31)	104.85(13)
C(11)–C(12)	1.382(4)	C(12)–C(11)–C(16)	119.23(31)
C(11)–C(16)	1.380(5)	C(11)–C(12)–C(13)	119.35(35)
C(12)–C(13)	1.411(5)	C(12)–C(13)–C(14)	120.36(37)
C(13)–C(14)	1.344(6)	C(13)–C(14)–C(15)	120.97(37)
C(14)–C(15)	1.374(6)	C(14)–C(15)–C(16)	119.37(37)
C(15)–C(16)	1.389(5)	C(11)–C(16)–C(15)	120.70(35)
C(21)–C(22)	1.380(4)	C(22)–C(21)–C(26)	118.82(30)
C(21)–C(26)	1.377(5)	C(21)–C(22)–C(23)	121.12(34)
C(22)–C(23)	1.384(5)	C(22)–C(23)–C(24)	119.15(36)
C(23)–C(24)	1.388(6)	C(23)–C(24)–C(25)	119.83(34)
C(24)–C(25)	1.371(6)	C(24)–C(25)–C(26)	120.44(36)
C(25)–C(26)	1.378(5)	C(21)–C(26)–C(25)	120.64(35)
C(31)–C(32)	1.385(4)	C(32)–C(31)–C(36)	118.57(28)
C(31)–C(36)	1.375(4)	C(31)–C(32)–C(33)	119.80(32)
C(32)–C(33)	1.397(5)	C(32)–C(33)–C(34)	120.30(35)
C(33)–C(34)	1.353(5)	C(33)–C(34)–C(35)	120.41(33)
C(34)–C(35)	1.360(5)	C(34)–C(35)–C(36)	120.02(35)
C(35)–C(36)	1.383(5)	C(31)–C(36)–C(35)	120.87(33)
C(41)–C(42)	1.350(9)	C(42)–C(41)–C(46)	119.85(56)
C(41)–C(46)	1.370(9)	C(41)–C(42)–C(43)	119.53(57)
C(42)–C(43)	1.388(8)	C(42)–C(43)–C(44)	119.79(52)
C(43)–C(44)	1.345(8)	C(43)–C(44)–C(45)	120.49(51)
C(44)–C(45)	1.356(8)	C(44)–C(45)–C(46)	120.11(54)
C(45)–C(46)	1.352(8)	C(41)–C(46)–C(45)	120.20(54)

[a] Symmetry related atom (−*x*, −*y*, −*z*).

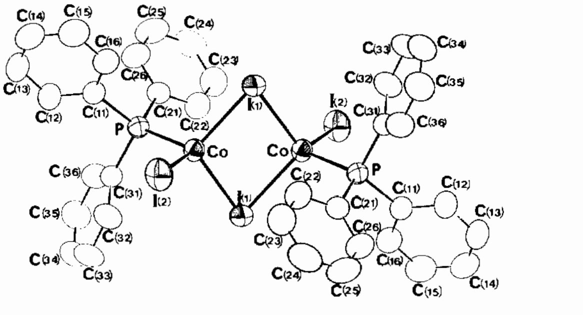

Fig. 1. ORTEP drawing of (a) $Co_2I_4(PPh_3)_2(C_6H_6)_2$ with thermal ellipsoids at 50% probability, showing the atomic numbering scheme. The hydrogen atoms and benzene molecules have been omitted.

TABLE V. Bond Distances and Other Significant Interatomic Distances (Å) and Angles for Compound (**b**) (e.s.d.s in the least significant digits in parentheses).

Co–I(1)	2.6471(7)	I(1)–Co–I(1)[a]	100.68(2)
Co–I(1)[a]	2.6521(7)	Co–I(1)–Co[a]	79.32(2)
Co–I(2)	2.5235(7)	I(1)–Co–I(2)	115.41(3)
Co–O	1.917(3)	I(1)–Co–O	103.08(11)
Co–Co[a]	3.382(1)	I(2)–Co–I(1)[a]	114.79(3)
I(1)–I(1)[a]	4.0795(6)	I(2)–Co–O	114.15(11)
I(1)–I(2)	4.3712(5)	O–Co–I(1)[a]	107.22(10)
I(2)–I(1)a	4.3606(4)	Co–O–P	137.46(22)
I(1)–O	3.603(3)	O–P–C(11)	109.81(23)
I(2)–O	3.742(4)	O–P–C(21)	106.41(22)
O–I(1)[a]	3.704(3)	O–P–C(31)	112.65(22)
O–P	1.522(3)		
P–C(11)	1.794(5)	C(11)–P–C(21)	108.51(24)
P–C(21)	1.788(5)	C(11)–P–C(31)	110.08(24)
P–C(31)	1.780(5)	C(21)–P–C(31)	109.23(24)
C(11)–C(12)	1.375(8)	C(12)–C(11)–C(16)	120.87(50)
C(11)–C(16)	1.400(7)	C(11)–C(12)–C(13)	118.38(57)
C(12)–C(13)	1.386(8)	C(12)–C(13)–C(14)	122.01(64)
C(13)–C(14)	1.353(10)	C(13)–C(14)–C(15)	120.19(59)
C(14)–C(15)	1.361(10)	C(14)–C(15)–C(16)	120.31(62)
C(15)–C(16)	1.408(8)	C(11)–C(16)–C(15)	118.21(57)
C(21)–C(22)	1.375(7)	C(22)–C(21)–C(26)	119.04(52)
C(21)–C(26)	1.392(8)	C(21)–C(22)–C(23)	121.28(57)
C(22)–C(23)	1.376(8)	C(22)–C(23)–C(24)	119.47(60)
C(23)–C(24)	1.376(10)	C(23)–C(24)–C(25)	120.22(59)
C(24)–C(25)	1.370(10)	C(24)–C(25)–C(26)	120.40(64)
C(25)–C(26)	1.389(9)	C(21)–C(26)–C(25)	119.50(59)
C(31)–C(32)	1.382(7)	C(32)–C(31)–C(36)	118.40(60)
C(31)–C(36)	1.395(7)	C(31)–C(32)–C(33)	120.44(53)
C(32)–C(33)	1.392(8)	C(32)–C(33)–C(34)	120.10(53)
C(33)–C(34)	1.354(8)	C(33)–C(34)–C(35)	120.24(54)
C(34)–C(35)	1.381(8)	C(34)–C(35)–C(36)	120.24(54)
C(35)–C(36)	1.366(8)	C(31)–C(36)–C(35)	120.57(51)
C(41)–C(42)	1.342(11)	C(42)–C(41)–C(46)	122.84(78)
C(41)–C(46)	1.348(11)	C(41)–C(42)–C(43)	117.83(83)
C(42)–C(43)	1.345(13)	C(42)–C(43)–C(44)	121.66(81)
C(43)–C(44)	1.382(15)	C(43)–C(44)–C(45)	118.04(80)
C(44)–C(45)	1.363(13)	C(44)–C(45)–C(46)	120.67(84)
C(45)–C(46)	1.350(11)	C(41)–C(46)–C(45)	118.93(77)

[a] Symmetry related atom (−*x*, 1 − *y*, −*z*).

[8] with an I···I distance of 4.15 Å. The Fe··Fe contact (3.05 Å) in this compound is much shorter, as in our Co-complexes (3.32 Å) (**a**) and 3.38 Å (**b**)). The geometry of the Co_2I_2 units thus appears to be determined by the iodide size.

The cobalt coordination sphere is completed by another iodide ion (2.51 and 2.52 Å, resp.), and the ligand donor atoms. The bond lengths are in the usual range (Co P = 2.36 Å; Co–O = 1.917 Å). In L_2CoCl_2 compounds (L = PPh_3 or $OPPh_3$) distances are given for Co–P = 2.38 Å and Co–O = 2.00 Å [11, 12].

Distortion of the tetrahedral coordination geometry depends on mutual repulsion of the different

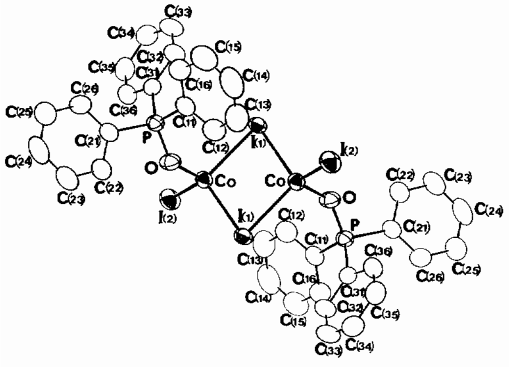

Fig. 2. ORTEP drawing of (b) $Co_2I_4(OPPh_3)_2(C_6H_6)_2$ with thermal ellipsoids at 50% probability, showing the atomic numbering scheme. The hydrogen atoms and benzene molecules have been omitted.

sized ligand atoms, because distances between all donor atoms are about equal to the sum of Van der Waals radii.

The P–C bond length and angles of the coordinated triphenylphosphine (a) are similar to other reported structures [11]. Also the analog triphenylphosphine oxide in (b) shows the well-known geometry from other coordination compounds as in $CoCl_2(OPPh_3)_2$ [12]. The C–C bond length and angles in the phenyl and benzene rings are in the usual range.

Intermolecular contacts are all greater than the Van der Waals distances; hence they support the premise that there are no unusual intermolecular interactions. The benzene molecules are thus present as lattice molecules without important interactions with the iodine atoms, and this explains their easy removal during thermogravimetric analysis.

TABLE VI. Main far-IR Stretching Bands for (a) and (b′) in cm^{-1}.[a]

	$[Co_2I_4(PPh_3)_2]$-$(C_6H_6)_2$	$[Co_2I_4(OPPh_3)_2]$-(C_6H_6)
$\bar{\nu}(Co-I)_{terminal}$	230s	212vs
$\bar{\nu}(Co-I)_{bridging}$	198vs	180vs
	184vs	158m
$\bar{\nu}(Co-P)$	115m	
$\bar{\nu}(Co-O)$		345m

[a] v = very; s = strong; m = medium.

Vibrational Spectra

The main far-infrared stretching bands are collected in Table VI. The presence of only one terminal $\bar{\nu}$(Co–I) and two bridging $\bar{\nu}$(Co–I) bands is in agreement with the C_{2h} symmetry of the $Co_2I_4P_2$ (a) or $Co_2I_4O_2$ (b) skeletons. A good inverse correlation is found between the mean values of the symmetric and asymmetric $\bar{\nu}$(Co–I) bridged vibrations and the corresponding bond lengths with 191 cm^{-1} and 2.62 Å for (a) and 169 cm^{-1} and 2.65 Å for (b). The same occurs between $\bar{\nu}$(Co–I) terminal and the corresponding bond length with 230 cm^{-1} and 2.515 Å for (a) and 212 cm^{-1} and 2.523 Å for (b).

The P–C distances are shorter in complex (b) (1.787 Å) than in complex (a) (1.818 Å). This observation can be related to the trend observed in the infra-red spectra [9] for the 'X sensitive' bands, which depend on the other phosphorus substituent. These bands are usually of higher energy in complex (b) than in complex (a).

Electronic spectra were consistent with a C_{3v} microsymmetry around cobalt(II) [9].

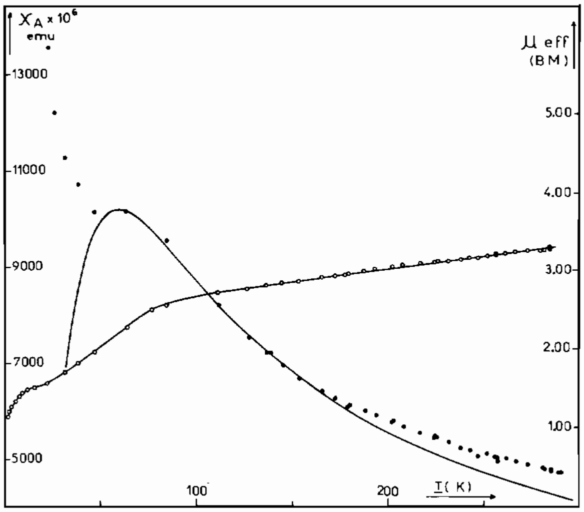

Fig. 3. Compound (a): Magnetic susceptibility (●) and magnetic moment (○) vs. Temperature and best fit for the susceptibility (solid line). Parameters given in Table VII.

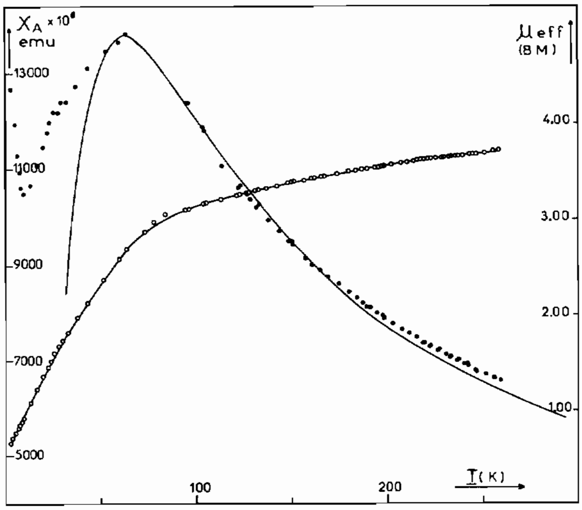

Fig. 4. Compound (b′): Magnetic susceptibility (●) and magnetic moment (○) vs. Temperature and best fit for the susceptibility (solid line). Parameters given in Table VII.

TABLE VII. Magnetic Data of $[(Co_2I_4(PPh_3)_2](C_6H_6)_2$ (a) and $[Co_2I_4(OPPh_3)_2](C_6H_6)$ (b′).

	μ_{eff} (BM) 293 K	θ (K) (300–100 K)	TIP 10^6 emu cgs	J (K)[a]	g
(a)	3.11	−170	660	−33	2.45
(b′)	3.75	−100	700	−35	2.95

[a] Determined for a limited T-range using $S = ½$ dimer.

Magnetism

The temperature dependance of the magnetic susceptibility and the effective magnetic moment are plotted in Figs. 3 and 4. The magnetic data are summarized in Table VII. The high negative Curie temperature values have been extrapolated from the linear dependence of the reciprocal values of the magnetic susceptibility *vs.* temperature between 300 K and 150 K for (a) and 300 K and 100 K for (b′); they support an antiferromagnetic interaction.

Antiferromagnetic interactions in dinuclear tetrahedral cobalt(II) complexes have previously been reported with monothiobenzoate ligand [13] and with phthalazine and pyrazine ligands [14].

The temperature dependent magnetic susceptibilities of the compounds were fitted to the Van Vleck equation found in the literature for intramolecular Heisenberg magnetic exchange effects in dinuclear systems [15]. Only in the case of a $S = ½$ dimer could a reasonable fit be obtained for the parameters given in Table VII. A plot of the susceptibility with a best fit for these parameters is given in Figs. 3 and 4. The quality of the fit is rather poor and therefore the values of J cannot be accurate. Small amounts of paramagnetic impurities, quite common in dimers [1, 2], influence the low temperature data strongly; at higher temperatures the thermal occupation of the upper levels of the $S = 3/2$ system became thermally populated. On the other hand, fitting with a $S = 3/2$ dimer gave much poorer results. It is evident that the interaction is strongly antiferromagnetic in both compounds.

Conclusion

The two described compounds are the first cases of tetrahedral dinuclear cobalt(II) with a double iodide bridge. The metal–metal distances are practically controlled by the iodine···iodine Van der Waals contacts. The triphenylphosphine or triphenylphosphineoxide have only a small influence on the geometries and on the magnetic properties. These structures contrast with another dinuclear complex $Co_2I_4(SPPh_3)_2$ where, according to spectroscopic properties, the triphenylphosphinesulfide ligands are in bridging positions and the iodine atoms are all in terminal positions [16].

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