respectively) while the P2–Rh–P4 and N12–Rh–N34 angles are opened to 103.9 (3) and 99.9 (8)°, respectively. The primed dication shows larger deviations from idealized square-pyramidal geometry around Rh′ (Table III and least-squares planes included as supplementary material[18]). This is not considered important and probably results from a difference in packing.

The two PNP ligands bridge the metal atoms, but the four P atoms are not coplanar as is commonly found in bis(phosphine)-bridged binuclear compounds.[12,24] The torsion angles P1–Au–Rh–P2 and P3–Au–Rh–P4 are −37 and 35°, respectively. The structure of **2** is very similar to that of $[Rh_2(CO)(\mu\text{-PNP})_2]^{2+}$ (**3**)[13] with the axial CO ligand removed. The corresponding torsion angles in **3** (P2–Rh1–Rh2–P3 and P1–Rh1–Rh2–P4) are −36 and 35°, respectively. The Au–P distances in **2** (average 2.300 (6) Å) are similar to values found in other gold–phosphine and mixed iridium–gold–phosphine clusters.[20-22] The Rh–P distances (average 2.217 (6) Å), which are trans to nitrogen atoms, are similar to values found in **3**.[13] The Rh–N bond distances in **2** (average 2.17 (2) Å) are similar to values found in **3** (2.15 (1) Å),[13] in $[Rh(nbd)PNP)]PF_6$ (2.15 Å),[11] and in $[Rh_2(CO)_2(\mu\text{-PNP})_2](PF_6)_2$ (2.19 Å).[12]

The average Au–Rh distance in **2** is 2.854 (2) Å. Since this is the first Rh–Au phosphine complex characterized by X-ray analysis, this distance cannot be compared to those in other similar compounds. However, several Ir–Au phosphine clusters have recently been subjected to X-ray analysis. In all of these compounds the Au–Ir distances are significantly shorter than the Au–Rh distance in **2**: $[(dppe)_2IrAuPPh_3](BF_4)_2$, 2.625 (1) Å;[25] $[(PPh_3)_3H_2Ir(\mu\text{-H})AuPPh_3]BF_4$, 2.765 (1) Å;[22] $[IrAu_2H(PPh_3)_4NO_3]BF_4$, 2.685 (1) Å.[21] The long distance in **2** is probably a result of the bridging PNP ligand.

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Registry No. **1**, 95936-60-0; **2**, 95936-62-2; $\mathbf{2}\cdot{}^1/_2C_3H_6O$, 95936-63-3; $[Rh(nbd)(PNP)]BF_4$, 86436-86-4; $Au(PPh_3)NO_3$, 14897-32-6; Au, 7440-57-5; Rh, 7440-16-6.

Supplementary Material Available: ^{31}P NMR spectrum of **2** and tables of positional and thermal parameters, least-squares planes, distances and angles, and observed and calculated structure factor amplitudes for **2** (45 pages). Ordering information is given on any current masthead page.

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Contribution from the Istituto di Teoria e Struttura Elettronica
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Synthesis, Characterization, and Magnetic Properties of the Linear-Chain Organic-Intercalated Chromium(II) Compound Tetramethylammonium Tribromochromate(II), $[(CH_3)_4N]CrBr_3$

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There has been a great deal of interest in the last few years in one-dimensional, 1D, transition-metal complexes, from both theoretical and experimental points of view, because they exhibit several unusual physical and chemical properties.[1,2]

In this context, the synthesis of new materials having quasi-1D physical properties appears to be an important challenge for a chemist.

Recently, we have synthesized and studied a series of two-dimensional ferromagnetic insulators of Cr(II), having general formula $(RNH_3)_2CrCl_4$, R = alkyl, whose structures are based on the tetragonal K_2NiF_4 lattice.[3,4] One of the salient chemical features of these Cr(II) compounds is that, when the bulkiness of the cation is increased, i.e. from the linear amine hydrochloride, RNH_3Cl, to the tetrahedral tetraalkylammonium chloride, R_4NCl, it is possible to obtain 1D Cr(II) compounds, having formula $[R_4N]CrCl_3$, where chains of Cr(II) octahedra, having faces in common, are present. Quite recently, in fact, we have described the synthesis, the crystal structure, and the magnetic properties of the first term of the series: tetramethylammonium trichlorochromate(II), $[(CH_3)_4N]CrCl_3$,[5] and we found that the compound shows 1D magnetic behavior and the crystal structure consists of linear chains of Cr(II) atoms bridged by three chloride ions.

In order to obtain more complete information on the physical properties of the series, we have carried out the synthesis of the corresponding bromide derivative. This note deals with the synthesis and the low-temperature magnetic behavior of tetramethylammonium tribromochromate(II), which shows antiferromagnetic exchange interactions.

Experimental Section

Tetramethylammonium bromide (BDH Chemical Ltd.) was used as supplied. Since the title compound is hygroscopic and very easily oxidized, the preparation and sample handling were carried out under nitrogen.[6]

Synthesis of $[(CH_3)_4N]CrBr_3$. Finely divided electrolytic chromium metal (0.647 g, 12.4 mmol) was placed in a three-necked 250-mL flask containing a Teflon-coated stirrer bar with 30 mL of glacial acetic acid, and nitrogen gas was bubbled for 20 min through the solvent. The chromium metal was completely dissolved by passing HBr gas under reflux, through the solvent, until a deep blue solution was obtained. The HBr addition was stopped, and a solution of $(CH_3)_4NBr$ (1.90 g, 12.4 mmol) in 50 mL of glacial acetic acid, degassed previously, was added dropwise to the Cr(II) solution. Immediately, a yellow crystalline product separated. The complex was then filtered and dried under vacuum with a Schlenk filtration apparatus.

The elemental analysis was performed by A. Bernhardt Mikroanalytische Laboratorium, Elbach, West Germany, and by Laboratorio Microanalisi, CNR, Area della Ricerca di Roma.

Anal. Calcd for $C_4H_{12}NCrBr_3$: C, 13.13; H, 3.30; N, 3.83; Cr, 14.21; Br, 65.52. Found: C, 13.07; H, 3.15; N, 3.85; Cr, 14.15; Br, 65.30.

X-ray Powder Diffraction. The polycrystalline sample was sealed under nitrogen in a Lindemann tube, i.d. 0.3 mm, and diffraction patterns were collected with a Philips Debye-Scherrer camera (Ni-filtered Cu Kα radiation).

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements in the temperature range 1.8–297 K were determined by using the Faraday apparatus described elsewhere.[7] The polycrystalline sample was placed inside a quartz sphere, sealed under nitrogen with a drop of "Durofix" glue, and suspended by a fine silica wire from a Sartorius electronic vacuum microbalance. The magnetic field and the gradient were supplied by two superconducting solenoids. The magnetization measurements were made at field strengths up to 7 T. Temperature measurements were based on a calibrated Au, 0.03% atomic Fe vs. chromel thermocouple and gallium arsenide diodes. Temperatures below 4.2 K were achieved by pumping on the liquid He in the inner Dewar of the Faraday balance.

Electronic Spectra. Near-infrared and visible spectra were taken on a Beckman DK 2A recording spectrophotometer. Powdered samples

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Table I. Powder X-ray Diffraction Data[a]

			$[(CH_3)_4N]CrCl_3$			$[(CH_3)_4N]CrBr_3$		
h	*k*	*l*	$1/d^2_{obsd}$, Å^{-2}	intens	$1/d^2_{calcd}$, Å^{-2}	$1/d^2_{obsd}$, Å^{-2}	intens	$1/d^2_{calcd}$, Å^{-2}
0	1	0	0.0165	vs				
1	0	1	0.0400	w	0.0396			
1	1	0	0.0484	vs	0.0480	0.0445	m	0.0452
2	0	1	0.0877	vs	0.0876	0.0812	vs	0.0819
0	0	2	0.0944	vw	0.0943	0.0869	m	0.0865
2	1	1	0.1371	w	0.1356	0.1281	s	0.1273
1	2	1						
3	0	0	0.1432	vw	0.1440			
2	0	2	0.1584	w	0.1583	0.1466	vw	0.1469
3	0	1	0.1692	vw	0.1676	0.1572	ms	0.1574
2	2	0	0.1939	vw	0.1920	0.1815	m	0.1811
3	1	0	0.2077	w	0.2080	0.1958	m	0.1962
1	3	0						
2	2	1	0.2097	w	0.2156			
3	0	2	0.2402	vw	0.2383	0.2223	mv	0.2233
3	2	0	0.3757	w	0.3040	0.2883	w	0.2883
2	3	0						

[a] Unit-cell parameters are given in the text.

were placed between two quartz glasses and sealed in a drybox, under nitrogen, with glue. MgO was used as reference. The absence of a broad intense band, centered at 450 nm, typical of Cr(III) impurities, was taken as a further purity check.

Results and Discussion

Tetramethylammonium tribromochromate(II), $[(CH_3)_4N]CrBr_3$, has been synthesized by a more convenient method,[8] by reaction of electrolytic chromium metal and HBr in glacial acetic acid and, after the dissolution of the chromium, by addition of a stoichiometric amount of the amine hydrobromide, dissolved in the same solvent. The yellow crystalline needlelike product separates immediately. The compound has been characterized by elemental analysis and by X-ray powder diffraction. The X-ray powder diffraction spectrum was indexed in the hexagonal space group $P6_3/m$ (C_{6h}^2). The data are reported in Table I together with those of the corresponding $[(CH_3)_4N]CrCl_3$, whose crystal structure has been solved.[5] The values of the unit-cell parameters, obtained by the least-squares method, are

$$a = b = 9.4_0\ \text{Å} \qquad c = 6.8_0\ \text{Å} \qquad \beta = 120°$$

The chloride derivative consists of infinite linear chains (along the *z* axis) of octahedral chromium atoms bridged by three chloride ions. The Cr–Cr distance inside the chain is 3.26 Å, (half the value of the *c* parameter of the unit cell). In the bromide derivative, assuming therefore the same crystal structure of $[(CH_3)_4N]CrCl_3$, the Cr–Cr distance should be 3.40 Å and that between the chains 9.40 Å. From the structural point of view, therefore, the bromide has longer *intra*chain and *inter*chain distances compared to those of the chloride derivative.

The near-infrared and visible spectrum of the title compound is characterized by an intense broad d–d band with a maximum at 9.7×10^3 cm^{-1} and a shoulder at $\sim 9 \times 10^3$ cm^{-1}. In the visible region, the absorption spectrum shows several weak bands, which are spin forbidden in nature. They arise from spin-forbidden quintet–triplet and quintet–singlet transitions, in agreement with the Tanabe–Sugano diagram for the high-spin octahedral Cr(II) ion. No intensity considerations can be made in the absence of single-crystal spectra as a function of temperature, and therefore no information on the collective nature of these transitions, i.e. exciton–magnon combination bands etc., can be obtained.[9]

The molar spin susceptibility $\chi_M{}^S$ was obtained from the measured static magnetic susceptibility corrected for the diamagnetic contribution and the temperature-independent paramagnetism, TIP. The first term was calculated by using Pascal's constants[10] and was found to be 1.075×10^{-4} emu/mol. The TIP was calculated from the usual expression, assuming that in O_h symmetry for Cr(II), $s = 2$, the ^{5}D splits to yield the ^{5}E$_g$ ground state:

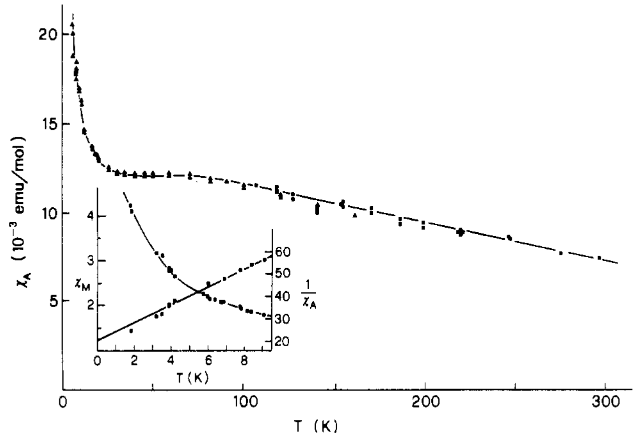

Figure 1. Molar magnetic susceptibility χ_M of $[(CH_3)_4N]CrBr_3$ as a function of temperature from 1.8 to 293 K.

$$\chi_{TIP} = 4N_a\mu_B{}^2/10Dq$$

where $10Dq \simeq 9000$ cm^{-1} from the electronic spectrum. The temperature dependence of $\chi_M{}^S$, from 1.8 K to room temperature is reported in Figure 1. At very high temperatures, $T \geqslant 250$ K, the susceptibility follows the Curie–Weiss law: $\chi_M = C/(T - \Theta)$, with $C = 3.14$ (corresponding to an effective moment $\mu_{eff} = 5.01$ μ_B), and $\Theta = -124$ K. In the temperature region $50 \leq T \leq 293$ K, the magnetic susceptibility shows a broad maximum centered at $T \simeq 70$ K. This maximum is characteristic of both antiferromagnetic linear-chain systems and isolated clusters. From X-ray powder data we can reasonably exclude the latter situation.

We then analyzed the magnetic susceptibility data in terms of the Smith–Friedberg equation[11] assuming the Heisenberg linear-chain model

$$\chi_M{}^S = \frac{N_a g^2 \mu_B{}^2 S(S+1)}{3k_B T}\ \frac{1+U}{1-U}$$

where $U = \coth K - 1/K$ and $K = 2JS(S+1)/k_BT$.

The χ_M vs. T curve was fitted with use of the above equation with $S = 2$ (see Figure 2), and the best values found for J and g were -13.15 K and 2.01, respectively. The negative value of the *intra*chain exchange constant coupling J shows that the exchange coupling inside the chain is definitely antiferromagnetic, in agreement with what has been observed in analogous Cr(II)

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Table II. Structural and Magnetic Parameters for $[CrCl_3]^-$ Chain Compounds

compd	M–M (intrachain), Å	M–B–M, deg	M–M′ (interchain), Å	Θ, K	J/k, K	T_N, K	g	$\|J'\|/\|J\|$	ref
$CsCrCl_3$	3.112	76.20	7.256		−24.0	16		3×10^{-3}	12
					−38.2		1.98		20
					−26.5		1.98		21
$[(CH_3)_4N]CrCl_3$	3.256	79.00	9.129	−158	−15.2	7		10^{-3}	5
$[(CH_3)_4N]CrBr_3$	3.40		9.40	−124	−13.1				this work

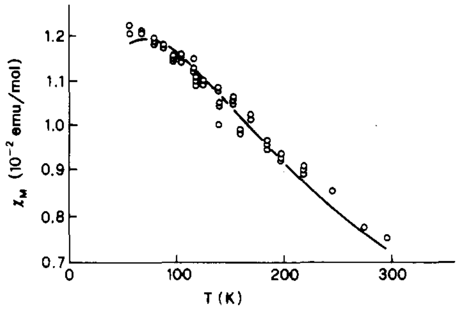

Figure 2. Molar magnetic susceptibility χ_M vs. temperature in the range 50 K to room temperature. The solid line is a fit of the data to the Smith and Friedberg equation.

complexes.[5,12-15] This behavior can be explained by assuming a direct overlap of the t_{2g} orbitals between the nearest-neighbor chromium(II) ions. The antiferromagnetic exchange can arise not only by direct overlap of the t_{2g} orbitals but also by a superexchange mechanism via e_g–s–e_g interactions. Ferromagnetic superexchange interactions involving the Br 4p orbitals are also present.[16] The fact that the overall interaction is antiferromagnetic indicates that the exchange is mainly due to the first two contributions. In addition, if we compare the J values, found in $CsCrCl_3$[12] and $[(CH_3)_4N]CrCl_3$[5] (compounds where the *intra*chain Cr–Cr distance increases from 3.11 to 3.26 Å) (see Table II), with that found in our compound (*intra*chain Cr–Cr distance 3.40 Å), we observe a decrease of the antiferromagnetic interactions, due to the decrease of the t_{2g}–t_{2g} direct overlap. On the other hand, the ferromagnetic superexchange contribution should become more important because there is an increase of chromium–halogen covalency, in going from the chloride to the bromide derivative.

Below 40 K, the magnetic susceptibility deviates considerably from that expected for an antiferromagnetic chain, and it increases steadily in value up to the lowest temperature accessible to us, i.e. 1.8 K. Magnetization measurements, at the same temperature, made in fields up to 7 T (see Figure 3) show a downward curvature at higher fields, but no saturation was reached. Similar behavior has been observed in other sensitive linear-chain compounds, and the suggestion has been made that it arises from magnetic impurities.[17] In the present case, one possible source of these impurities may be a very small fraction of ferromagnetic $CrBr_3$ (T_c = 36 K),[18] but this possibility can be ruled out because no saturation was observed. The other possibility is the presence of paramagnetic impurities (estimated to be on the order of 3%).[19]

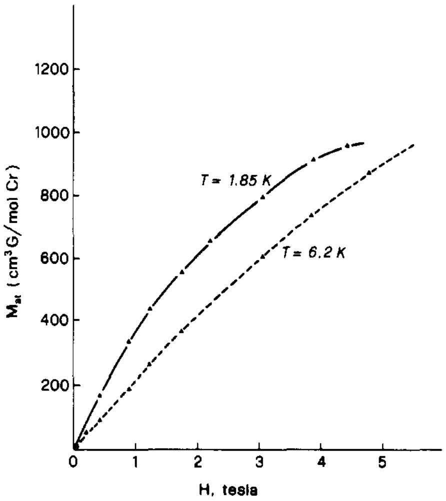

Figure 3. Magnetization vs. external magnetic field of $[(CH_3)_4N]CrBr_3$ at 1.8 K (-Δ-Δ) and 6.2 K (---Δ---Δ).

The three-dimensional magnetic ordering temperature, T_N, has not been detected, possibly due to the masking effect of the impurities. The temperature T_N, if present, is expected to lie below 7 K, the observed value for $[(CH_3)_4N]CrCl_3$,[5] and this is because of the presence of a longer *inter*chain distance.

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Registry No. $[(CH_3)_4N]CrBr_3$, 29794-92-1; Cr, 7440-47-3; HBr, 10035-10-6.

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Direct Observation of the Boron-Boron Coupling and High-Resolution Proton and Boron Spectra of Diborane

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Proton and boron-11 spectra of diborane have been previously reported,[1-4] but by today's standards, the resolution was limited. Useful experimental evidence was, however, obtained for the direct ^{11}B–^{10}B spin coupling constant.[1,2,4] Reasonably accurate estimates of the coupling constants not directly observable were obtained by fitting observed and computer-calculated ^1H and ^{11}B spectra.[1,2] The quality of these estimates was limited because of the dispersion and resolution of early spectrometers. The direct ^{11}B–^{11}B coupling

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