

Molecular and Crystal Structure of the Complex Composed of 2,3,5-Triphenyltetrazolium Cation and Dichloro(1,3,5-triphenylformazanato)cobaltate(II) Anion

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Abstract

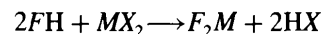
The molecular and crystal structure of cobalt(II) complex prepared by the reaction of 1,3,5-triphenylformazan with cobalt dichloride, dichloro(1,3,5-triphenylformazanato)cobaltate(II), has been determined by means of X-ray diffraction. The complex crystallized in a triclinic space group $P\bar{1}$, with $M_r = 728.55$, $a = 10.214(3)$, $b = 18.208(7)$, $c = 9.985(2)$ Å, $\alpha = 96.44(3)$, $\beta = 107.92(2)$, $\gamma = 81.79(3)^\circ$, $Z = 2$, $D_x = 1.387$ Mg m⁻³, $\mu = 0.683$ mm⁻¹, $F(000) = 750$, $R = 0.041$, $wR = 0.040$ and $S = 1.40$. The complex is composed of a pair of ions, the 2,3,5-triphenyltetrazolium cation and the dichloro(1,3,5-triphenylformazanato)cobaltate(II) anion. The cobalt(II) ion is tetrahedrally coordinated by two N atoms and two chloride ions. One of the chloride ions of the anion has electrostatic intermolecular contacts with the tetrazolium ring of the cation. The conductivity of the complex in nitromethane solution showed complete dissociation of a pair of ions to separate ions.

1. Introduction

Formazans have been of interest because they are easily oxidized to the corresponding tetrazolium ions (Fig. 1). This process brings about such a drastic change in color that it has been applied as a test of the oxidation–reduction ability in living tissues (Ninham, 1955). Formazans have been known to make complexes with transition-metal ions. The combination of their oxidizing and complex-forming properties seemed to result in complicated reactions (Price, 1967, 1971; Witter, 1968). However, formulation of the products was described mainly based upon the result of elemental analyses and optical absorption (Grün & Feiesleben, 1958; Irving, Gill & Cross, 1960). The electron configuration of the complexes has been discussed, referring to the formulation and the optical absorption. Only a few papers have been concerned with their structures and magnetic properties (Balt, Renkema, Van Capellveen & Stam, 1976;

Siedle & Pignolet, 1980; Ermakova, Kryko & Postarsky, 1960).

The authors have carried out magnetic and ESR spectroscopic studies regarding several kinds of complexes formed by formazans with such transition-metal ions as copper, nickel and cobalt. The results indicated a full variety of magnetic characteristics of the complexes (Kawamura, Yamauchi & Ohya-Nishiguchi, 1993; Kawamura & Yamauchi, 1995). However, the complex formulation was still described using the results of the elemental analysis. Most of the complexes were considered to be neutral formazanato complexes, following the reaction in the literature (Jerchel & Fischer, 1954; Irving, Gill & Cross, 1960).



Here, the formazanato anion and divalent metal ion are abbreviated as F^- and M^{2+} . On the other hand, the tetrazolium cation necessitates an anion (Waender & Russell, 1966). In the complex where neutral formazans coordinate to the copper(I) ion, counter anions were found (Balt, Renkema, Van Capellveen & Stam, 1976). For complexes with this variable formazan ligand, X-ray analysis was necessary for definite structural determination.

This is the first report clarifying the coexistence of the complex anion of dichloro(1,3,5-triphenylformazanato)cobaltate(II) and the tetrazolium cation using X-ray analysis.

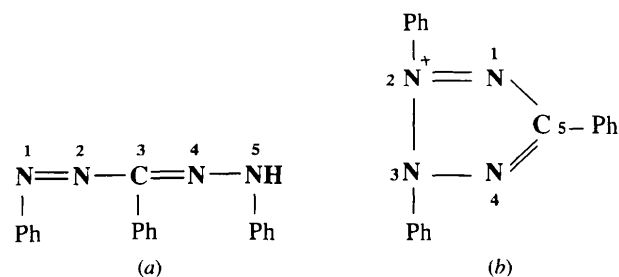


Fig. 1. Molecular formulae of (a) 1,3,5-triphenylformazan and (b) 2,3,5-triphenyltetrazolium.

2. Experimental

2.1. Material preparation

1,3,5-Triphenylformazan (1 g) and anhydrous cobalt dichloride (0.6 g) in ethanol (20 ml) were kept standing for 1 week at room temperature. Black prismatic crystals (0.74 g) were precipitated. The crystals were then washed with acetone: 2,3,5-triphenyltetrazolium dichloro(1,3,5-triphenylformazanato)cobaltate(II) (1), $[N=NPh-NPh-N=CPh]^+ \cdot [CoCl_2(NPh=N-CPh=N-NPh)]^-$. Found: C 62.98, H 4.07, N 15.29; calc. for $C_{38}H_{30}N_8CoCl_2$: C 62.59, H 4.12, N 15.37%. Here, the anionic part of the complex, the dichloro(1,3,5-triphenylformazanato)cobaltate(II) anion, is indicated by (2).

2.2. Crystallographic measurement and calculation

The crystal data and experimental details are summarized in Table 1.

All calculations were carried out on a VAX station 3200 with the *TEXSAN* programs (Molecular Structure Corporation, 1985). The atomic scattering factors (f , f' and f'') were taken from *International Tables for X-ray Crystallography* (Cromer, 1974).^{*} All the measurements and calculations were carried out at the Advanced Instrumentation Centre of Chemical Analysis, Ehime University, Japan.

2.3. Magnetic measurements

Magnetic susceptibility measurements were carried out with a SQUID magnetometer (Quantum Design Inc., Model MPMS-2) in the temperature range between room temperature and 77 K. The ESR spectra were measured on a JEOLCO-1XG equipped with 100 kHz field modulation.

3. Results and discussion

3.1. Molecular structure

Atomic parameters with an equivalent temperature factor B_{eq} are tabulated in Table 2. The molecular structure with atomic numbering system is illustrated in Fig. 2. Selected bond lengths and angles are tabulated in Table 3. The four N atoms in the formazan chelate are coplanar, within experimental error; hereafter, this plane is referred to as the formazan N plane. The cobalt(II) ion and C1 atom are shifted 0.244 (3) and 0.089 (3) Å, respectively, from the formazan N plane. Two pairs of bonding, N1—N2 and N3—N4, and N2—C1 and C1—N3, are equivalent.

^{*}Lists of atomic coordinates, anisotropic displacement parameters, complete geometry and structure factors have been deposited with the IUCr (Reference: OA0004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Experimental details

Crystal data	
Chemical formula	$(C_{19}H_{15}N_4)^+ \cdot [Co(C_{19}H_{15}Cl_2N_4)]^-$
Chemical formula weight	728.55
Cell setting	Triclinic
Space group	$P\bar{1}$
a (Å)	10.214 (3)
b (Å)	18.208 (7)
c (Å)	9.985 (2)
α (°)	96.44 (3)
β (°)	107.92 (2)
γ (°)	81.79 (3)
V (Å ³)	1744 (1)
Z	2
D_c (Mg m ⁻³)	1.387
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71069
No. of reflections for cell parameters	24
θ range (°)	12.75–12.95
μ (mm ⁻¹)	0.683
Temperature (K)	298
Crystal form	Prismatic
Crystal size (mm)	0.45 × 0.35 × 0.20
Crystal color	Black
Data collection	
Diffractometer	Rigaku AFC-5R
Data collection method	ω -2 θ scans
Absorption correction	ψ scans of five reflections (North, Phillips & Mathews, 1968)
T_{min}	0.97
T_{max}	1.00
No. of measured reflections	8474
No. of independent reflections	8020
No. of observed reflections	4186
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int}	0.029
θ_{max} (°)	27.5
Range of h, k, l	0 → h → 13 -23 → k → 23 -12 → l → 12
No. of standard reflections	3
Frequency of standard reflections	Every 150 reflections
Intensity decay (%)	0.15
Refinement	
Refinement on	F
R	0.041
wR	0.040
S	1.40
No. of reflections used in refinement	4186
No. of parameters used	443
H-atom treatment	H atoms placed in idealized positions (C—H 0.95 Å) with $B_{iso} = 1.2B_{eq}(C)$
Weighting scheme	$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$	0.0002
$\Delta\rho_{max}$ (e Å ⁻³)	0.37
$\Delta\rho_{min}$ (e Å ⁻³)	-0.26
Extinction method	Secondary
Extinction coefficient	3.50×10^{-7}
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

The atomic deviations of C2, C14 and C8 atoms from this N plane are -0.216 (3), 0.284 (3) and 0.272 (3) Å, respectively, where the positive sign corresponds to the same deviation as the cobalt(II) ion. The chloride ions deviate much from this molecular plane, forming a tetrahedral conformation around the cobalt(II) ion. It is noted that the two Co—N bond lengths are equivalent. However, the Co—Cl(1) bond is significantly longer

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Co	0.28689 (5)	0.21755 (3)	0.13490 (5)	3.10 (2)
Cl(1)	0.4507 (1)	0.18132 (6)	0.3326 (1)	4.63 (5)
Cl(2)	0.0756 (1)	0.19094 (6)	0.1234 (1)	4.38 (5)
N1	0.2797 (3)	0.3218 (2)	0.0991 (3)	3.0 (1)
N2	0.3218 (3)	0.3456 (2)	0.0010 (3)	3.1 (1)
N3	0.3680 (3)	0.2240 (2)	-0.1200 (3)	3.4 (1)
N4	0.3295 (3)	0.1831 (2)	-0.0419 (3)	3.2 (1)
N5	-0.2151 (3)	0.1864 (2)	-0.1555 (3)	3.7 (1)
N6	-0.2605 (3)	0.2086 (2)	-0.0466 (3)	3.7 (1)
N7	-0.1645 (3)	0.3001 (2)	-0.0991 (3)	3.4 (1)
N8	-0.1584 (3)	0.2421 (2)	-0.1880 (3)	3.4 (1)
C1	0.3702 (4)	0.2975 (2)	-0.0902 (3)	3.1 (2)
C2	0.2223 (4)	0.3819 (2)	0.1765 (4)	3.2 (2)
C3	0.2197 (4)	0.3703 (2)	0.3101 (4)	4.3 (2)
C4	0.1673 (5)	0.4265 (3)	0.3895 (4)	5.0 (2)
C5	0.1167 (4)	0.4947 (2)	0.3376 (5)	5.0 (2)
C6	0.1179 (4)	0.5063 (2)	0.2048 (5)	4.6 (2)
C7	0.1697 (4)	0.4503 (2)	0.1236 (4)	4.0 (2)
C8	0.4337 (4)	0.3340 (2)	-0.1786 (3)	3.2 (2)
C9	0.4761 (4)	0.4041 (2)	-0.1365 (4)	3.9 (2)
C10	0.5430 (4)	0.4363 (2)	-0.2128 (4)	4.9 (2)
C11	0.5655 (4)	0.3994 (3)	-0.3326 (4)	5.1 (2)
C12	0.5221 (4)	0.3308 (3)	-0.3768 (4)	4.6 (2)
C13	0.4569 (4)	0.2973 (2)	-0.3011 (4)	3.6 (2)
C14	0.3155 (4)	0.1085 (2)	-0.1012 (4)	3.5 (2)
C15	0.2926 (5)	0.0888 (2)	-0.2431 (4)	5.3 (2)
C16	0.2819 (6)	0.0149 (3)	-0.2930 (5)	6.9 (3)
C17	0.2931 (5)	-0.0384 (2)	-0.2028 (5)	6.0 (3)
C18	0.3127 (5)	-0.0189 (2)	-0.0632 (5)	5.8 (2)
C19	0.3243 (5)	0.0546 (2)	-0.0119 (4)	4.9 (2)
C20	-0.2274 (4)	0.2787 (2)	-0.0118 (4)	3.4 (2)
C21	-0.2167 (4)	0.1113 (2)	-0.2199 (4)	3.9 (2)
C22	-0.0944 (5)	0.0677 (2)	-0.2082 (5)	5.2 (2)
C23	-0.1001 (5)	-0.0056 (3)	-0.2621 (6)	6.6 (3)
C24	-0.2249 (6)	-0.0330 (2)	-0.3213 (5)	5.8 (3)
C25	-0.3443 (5)	0.0114 (3)	-0.3299 (5)	5.6 (2)
C26	-0.3430 (4)	0.0850 (3)	-0.2787 (4)	5.1 (2)
C27	-0.2545 (4)	0.3250 (2)	0.1073 (4)	3.8 (2)
C28	-0.3419 (4)	0.3034 (2)	0.1757 (4)	4.2 (2)
C29	-0.3708 (4)	0.3491 (3)	0.2850 (4)	5.2 (2)
C30	-0.3132 (5)	0.4137 (3)	0.3285 (4)	5.8 (2)
C31	-0.2249 (5)	0.4348 (3)	0.2624 (5)	5.9 (2)
C32	-0.1952 (4)	0.3903 (2)	0.1524 (4)	4.9 (2)
C33	-0.0996 (4)	0.2404 (2)	-0.3025 (4)	3.5 (2)
C34	0.0180 (4)	0.2751 (2)	-0.2743 (4)	4.2 (2)
C35	0.0732 (4)	0.2778 (3)	-0.3845 (5)	5.3 (2)
C36	0.0113 (5)	0.2456 (3)	-0.5161 (4)	5.5 (2)
C37	-0.1053 (5)	0.2112 (3)	-0.5403 (4)	5.5 (2)
C38	-0.1642 (4)	0.2086 (2)	-0.4338 (4)	4.6 (2)

Table 3. Selected geometric parameters (\AA , $^\circ$)

Co—Cl(1)	2.251 (1)	N4—C14	1.427 (4)
Co—Cl(2)	2.245 (1)	C1—C8	1.500 (4)
Co—N1	1.957 (3)	N5—N6	1.311 (4)
Co—N4	1.961 (3)	N5—N8	1.351 (4)
N1—N2	1.318 (3)	N5—C21	1.443 (5)
N1—C2	1.430 (4)	N6—C20	1.348 (4)
N2—C1	1.348 (4)	N7—N8	1.309 (4)
N3—N4	1.313 (3)	N7—C20	1.348 (4)
N3—C1	1.339 (4)	N8—C33	1.442 (4)
Cl(1)—Co—Cl(2)	112.82 (5)	N2—C1—N3	132.2 (3)
Cl(1)—Co—N1	114.65 (9)	N2—C1—C8	113.5 (3)
Cl(1)—Co—N4	115.21 (9)	N3—C1—C8	114.2 (3)
Cl(2)—Co—N1	110.44 (9)	N6—N5—N8	109.6 (3)
Cl(2)—Co—N4	110.33 (9)	N6—N5—C21	123.5 (3)
N1—Co—N4	91.6 (1)	N8—N5—C21	126.7 (3)
Co—N1—N2	125.6 (2)	N5—N6—C20	104.3 (3)
Co—N1—C2	122.6 (2)	N8—N7—C20	104.3 (3)
Co—N4—N3	125.7 (2)	N5—N8—N7	109.8 (3)
Co—N4—C14	121.3 (2)	N5—N8—C33	126.8 (3)
N2—N1—C2	111.8 (3)	N7—N8—C33	123.4 (3)
N1—N2—C1	121.2 (3)	N6—C20—N7	111.9 (3)
N4—N3—C1	121.3 (3)	N6—C20—C27	123.7 (3)
N3—N4—C14	112.9 (3)	N7—C20—C27	124.3 (3)

Two phenyl rings, including C2 and C14 atoms, are twisted by approximately the same angle around the bonds connecting them to the central chelate ring; these torsion angles are $23.7(5)^\circ$ and $-23.9(5)^\circ$, respectively. Hereafter, these phenyl rings are abbreviated as the C2 phenyl ring and C14 phenyl ring *etc.* The torsion angle of the C2 phenyl ring is defined as the average of the four torsion angles C3—C2—N1—Co, C7—C2—N1—N2, C3—C2—N1—N2 and C7—C2—N1—Co. The following torsion angles of the other phenyl rings are similarly defined. The torsion angle of the C8 phenyl ring is $16.7(5)^\circ$. This torsion means the complex anion deviates from C_2 symmetry, although the chelate ring itself keeps approximately C_2 symmetry. A similar molecular structure can be observed in

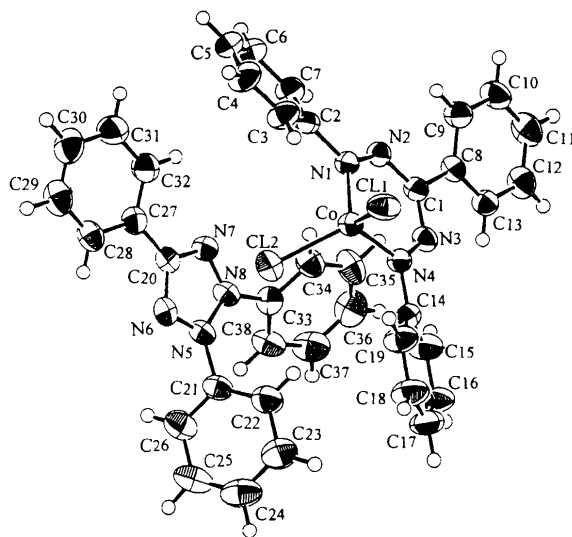


Fig. 2. ORTEP drawing of 2,3,5-triphenyltetrazolium dichloro(1,3,5-triphenylformazanato)cobaltate(II) with 50.0% probability ellipsoids, showing the labeling scheme.

than the Co—Cl(2) bond. The bond angles Cl(1)—Co—N1 and Cl(1)—Co—N4 are greater than Cl(2)—Co—N1 and Cl(2)—Co—N4. These bond lengths and angles describe a slightly distorted tetrahedral geometry around the cobalt(II) ion.

The bond angles around the five atoms of the formazan N plane are almost 120° . This fact suggests sp^2 hybridization and, at the same time, the coplanarity of these five atoms. Furthermore, each pair of bondings, N1—N2 and N3—N4, N2—C1 and C1—N3, and N1—Co and N4—Co, is equivalent, indicating the conjugation of five atoms of the chelate ring. These findings suggest that proton elimination is reasonable in chelate ring formation.

the 2,4,6-triphenylverdazyl radical and its methyl and chloro derivatives, in which the bridging group is methylene ($-\text{CH}_2-$) rather than the $-\text{CoCl}_2-$ in the present complex anion (Williams, 1973; Azuma, Deguchi, Marumo & Saito, 1975; Azuma, 1980).

The five atoms in the tetrazolium ring are also coplanar. The plane defined by the ring is referred to as the tetrazolium N plane. Two pairs of bonds, N5—N6 and N7—N8, and N5—C20 and C20—N8, are equivalent. The N5—N8 bond, however, is much longer than the former two bonds. The elongation of this bond may be ascribed to the repulsion between the relevant phenyl groups. The deviations of the C21, C33 and C27 atoms from the tetrazolium N plane are 0.124 (3), -0.028 (3) and 0.048 (3) Å, respectively. The torsion angles of C21, C27 and C33 phenyl rings are 62.4 (5), -11.9 (5) and -40.7 (5)°, respectively. Therefore, a propeller-like conformation is not observed in the tetrazolium cation.

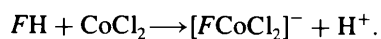
3.2. Molecular packing

The chloride ion Cl(2) in the $[CoCl_2(NPh=N-CPh=N-NPh)]$ anion has short intermolecular contacts with the tetrazolium ring in the 2,3,5-triphenyl-tetrazolium cation; the distances from Cl(2) to C20, N6, N7, N5 and N8 atoms, 3.233 (4), 3.315 (3), 3.339 (3), 3.392 (3) and 3.418 (3) Å, respectively, are shorter than the sum of the van der Waals radii of the two atoms. The McLachlan calculation for the tetrazolium cation (parameters used: $\alpha_N = 0.8\alpha$, $\beta_{NN} = 0.8\beta$ and $\beta_{NC} = 0.8\beta$) gave π -electron densities of 1.223, 1.397 and 0.843 e \AA^{-3} on N5, N6 and C20 atoms (McLachlan, 1960). The result indicates that the positive charge is almost localized on the central five-membered ring, especially on the N5, N6 and C20 atoms. The π -electron densities on all the phenyl C atoms were close to 1.0 e \AA^{-3} . Therefore, the intermolecular contacts within the ion pair above described may be ascribed to the electrostatic interaction between the Cl(2) ion and the tetrazolium ring. All these intermolecular contacts are ascribed to those within the ion pair. On the other hand, another chloride ion, Cl(1), has no contacts with any other atoms shorter than 3.7 Å; the shortest is 3.764 (5) Å, between the ion and C24 in another ion pair with the symmetry operation $-x, -y, -z$. Therefore, the ion pairs are packed discretely, as illustrated in Fig. 3. The finding that the magnetic moment of the complex did not change down to 77 K, within experimental error, explains well the packing of the ion pairs.

3.3. Characterization of (1)

The result of the elemental analysis indicated that the cobalt(II) ion and the original formazan reacted with stoichiometry 1:2 on creating the present complex. The stoichiometry is similar to that of many formazan-transition-metal complexes. The result of the X-ray

analysis revealed that the 2,3,5-triphenyltetrazolium cation exists in the complex. Since the tetrazolium cation is univalent and no other ion is apparently found in the crystal, the anionic moiety of the complex has to be univalent in order to keep the electrical neutrality. On the other hand, the magnetic moment of (1) was $4.0 \mu_B$ in the temperature range of the magnetic susceptibility measurements and corresponded to a spin state of 3/2. Therefore, the cobalt ion is divalent in the anionic moiety, because this spin state of the cobalt ion is only realized by the divalent cobalt ion with d^7 electron configuration. On creating the anionic moiety, one molecule of formazan would have removed one proton to make the 1,3,5-triphenylformazanato anion. Also, the anion and two chloride ions coordinate to the cobalt(II) ion to yield the dichloro(1,3,5-triphenylformazanato)cobaltate(II) anion (2), as described by the scheme



The coordinations accompanied with proton elimination have been found in many complexes (Assour, 1956; Assour & Kahn, 1965). Thus, the coordination of the formazanato ion to the cobalt(II) ion, without any proton, has been justified.

The present complex is characteristic with respect to coordination and construction compared with other formazan-transition-metal complexes. The elemental analysis of the complex was in good agreement with that of the complex obtained by Price (1967). However, the coordination and crystal character were different from

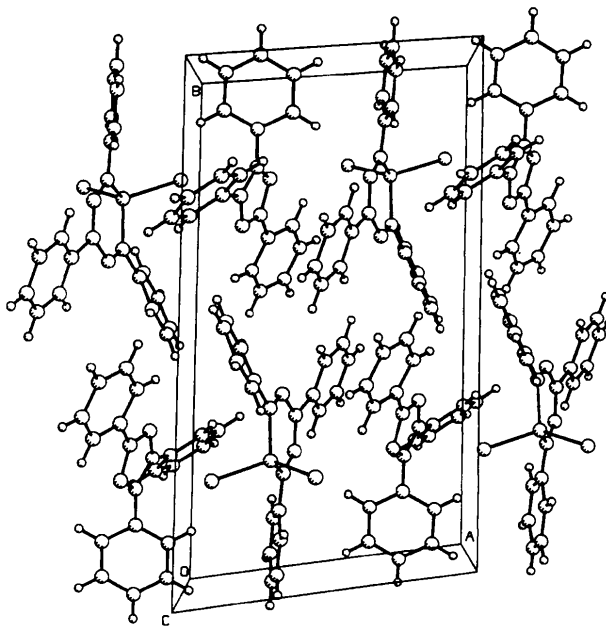


Fig. 3. Crystal packing of 2,3,5-triphenyltetrazolium dichloro(1,3,5-triphenylformazanato)cobaltate(II).

his complex, which was not ionic and in which the cobalt(II) ion was coordinated by two chloride ions and four N atoms of two formazan molecules. On the other hand, the coordination of formazanato ions to Pd(II) ion, by the N1 and N4 atoms of the ions, and that of formazans to the Cu(I) ion, by the N1 and N3 atoms of the molecules, have been reported (Siedle & Pignolet, 1980; Balt, Renkema, Van Capellveen & Stam, 1976). On complex formation as mentioned above, formazan molecules behaved uniformly. However, in the present case only one part of the formazans coordinated to the cobalt(II) ion as the formazanato anion, the other part was oxidized to the corresponding tetrazolium cation to construct ion pairs. Complex formation accompanying the oxidation of 1,3,5-triphenylformazan was not recognized during the reaction with cobalt(II) acetate, but recognized with cobalt(II) dichloride.

In the complex of bis(2,3,5-triphenyltetrazolium)-tetrachlorocobaltate(II) (3), the cobalt(II) ion is reputed to be coordinated by four chloride ions to make a divalent anion, tetrachlorocobaltate(II), and two ions of tetrazolium exist for each anion. In that case, the tetrazolium cation was easily estimated from the absorption spectra, since the absorptions were

mainly due to the anion (Goodgame & Cotton, 1962). The magnetic moment of complex (3) was $5.0 \mu_B$, which corresponded to a spin state of 3/2 for the cobalt(II) ion, indicating that a tetrahedral geometry around the cobalt(II) ion is realized in the complex. However, when the two ions, the formazanato anion and the tetrazolium cation, coexist, it would be quite difficult to assume the molecular formulation from the absorption spectra. In contrast with complex (3), the geometry around the cobalt(II) ion in the complex bis(1,3,5-triphenylformazanato)cobalt(II) (4) was assumed to be planar, from the magnetic moment of $1.8 \mu_B$ and g value obtained by ESR measurements (Kawamura, Yamauchi & Ohya-Nishiguchi, 1990). The cobalt(II) ion was regarded as coordinated by four N atoms of two formazanato ions to form the neutral complex. The anionic moiety of (2), taking an intermediate coordination between (3) and (4), also had an intermediate univalent negative charge. Interestingly, the spin state and geometry of (2) corresponded to those of (3).

The molar conductivity in $1.0 \times 10^{-3} M$ nitromethane solution of (1) was $62.2 \Omega^{-1} \text{cm}^2$ at 298 K, showing the ionic character in a nitromethane solution of the complex. In addition, the conductivity of these solutions did not show any concentration dependency at 298 K, indicating that the complex is completely dissociated to the ions. This finding suggests that the electrostatic interaction between the two types of ions is weaker than solvation with nitromethane. As shown in Fig. 4, the ESR spectra of (1) in the microcrystalline state and in a dichloromethane solution were different, suggesting different ESR parameters. Dissociation of the ion pair would occur in solution, as suggested by the conductivity.

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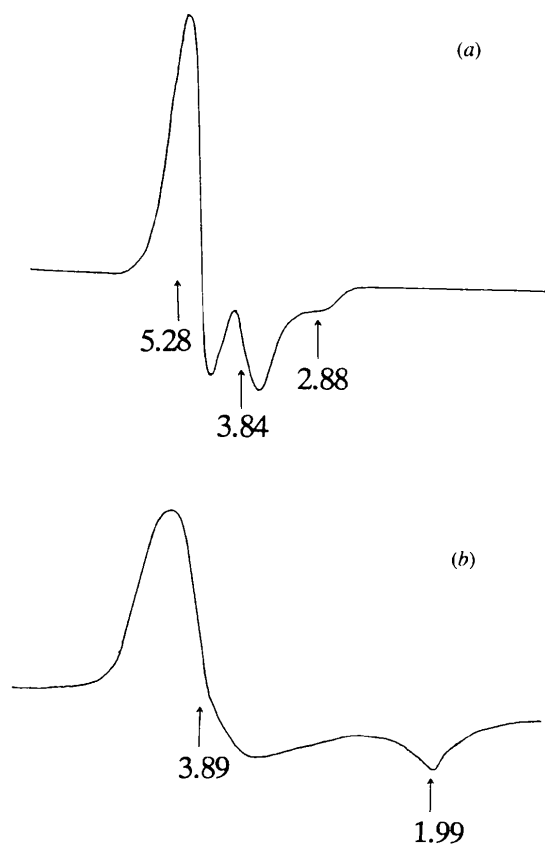


Fig. 4. ESR spectra of (a) at 4.2K: (1) in the microcrystalline state and (b) in dichloromethane solution (g values are indicated on the spectra).

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