Electronic Spectra of Square-Planar Bis(biuretato)cobaltate(III)-Type Complexes

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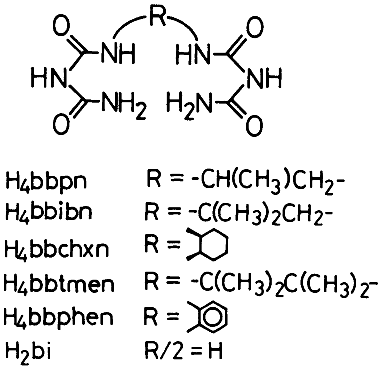
Several square-planar cobalt(III) complexes of bis(biuretato)-type were synthesized with new quadridentate ligands, alkylenebis(biuret)'s, where alkylene bridging group is (*R*,*S*)- or (*R*)-propylene, 1,1-dimethylethylene, *cis*-1,2-cyclohexylene, or tetramethylethylene. Faraday parameters for possible CT transitions in the complexes were expressed as functions of MO coefficients and energies. From the examination of the magnetic circular dichroism, the intense absorption band observed at ca. 20×10³ cm⁻¹ was assigned to ligand-to-metal charge-transfer transitions of ligand π (a_u of D_{2h}) to metal d_{yz} and $d_{zx'}$, and the ground state was inferred to be one close to D_{4h} symmetry. The band assignment was also consistent with the resonance Raman spectrum of potassium bis(biuretato)cobaltate(III). Absorption spectra of the complexes occasionally lost intensity with decrease of temperature. Origin of the thermochromism, which was found to be reversible, was also discussed.

Bis(biuretato)cobaltate(III)-type complexes, first reported by Bour and Steggerda, are known to possess a square-planar $Co(N)_4$ coordination geometry.[1–3] Magnetic susceptibility measurements have shown that spin-triplet ground state is retained even below 10 K in crystalline state.[4] The electronic ground state and the coordination mode have been considered to be kept also in solution as judged by observed electronic spectral features. To our knowledge, no detailed investigations have ever been made, however, about the interactions of the complexes with the solvent molecules of weak electron-donor property such as dimethyl sulfoxide (DMSO), ethanol, and water, though some amines have been demonstrated to be coordinated to give usual low-spin six-coordinate cobalt(III) species in ethanol.[4] Consistently potassium bis(3-phenylbiuretato)cobaltate(III) crystallizes with two uncoordinated DMSO molecules as revealed by X-ray analysis.[3]

Furthermore, nature of electronic absorption bands in the complexes have been not so fully investigated. In the present paper, the following main points will be discussed: 1) Assignment of the relatively weak and intense absorption bands observed at 10—16 and ca. 20×10³ cm⁻¹, respectively. 2) A remarkable thermochromism in water-containing media, which was discovered in the present study.

Scheme 1 displays the ligands used and their abbreviations. The complexes with the last two ligands are known[4] whereas complexes with the other four were newly prepared for the purpose of comparative study of their electronic spectra. Improvement of solubility properties was achieved to some extent by the modification of ligands in the complexes.



Scheme 1.

Experimental

Materials. *o*-Phenylenebis(biuret) (H_4bbphen) and three new ligands, (*R*,*S*)-propylene-, 1,1-dimethylethylene-, and *cis*-1,2-cyclohexylene-bis(biuret) (H_4bbpn, H_4bbibn, and H_4*cis*-bbchxn) were prepared in a similar manner as given for H_4bbphen:[4] For the new ligands, mp 201—202, 207—208, 199.5—200.5 °C, respectively. Found for $H_4bbpn \cdot 2H_2O$: C, 29.78; H, 6.52; N, 29.47%. Calcd for $C_7H_{18}N_6O_6$: C, 29.79; H, 6.43; N, 29.77%. Found for H_4bbibn: C, 36.68; H, 6.16; N, 31.82%. Calcd for $C_8H_{16}N_6O_4$: C, 36.92; H, 6.20; N, 32.29%. Found for H_4*cis*-bbchxn·$0.5H_2O$: C, 40.79; H, 6.42; N, 28.45%. Cacld for $C_{10}H_{19}N_6O_{4.5}$: C, 40.67; H, 6.49; N, 28.46%. (*R*)-Propylenebis(biuret) was similarly derived from (*R*)-propylenediamine. Found for $H_4bbpn \cdot 2H_2O$: C, 29.59; H, 6.60; N, 29.44%.

Tetramethylethylenebis(biuret) (H_4bbtmen) was also obtained by a similar procedure, but we often found that *N*,*N*-dimethylformamide (DMF) was preferred as solvent for the syntheses of alkylbiurets,[5] especially in this case: mp 210—210.5 °C. Found for H_4bbtmen: C, 41.67; H, 7.00; N, 28.81%. Calcd for $C_{10}H_{20}N_6O_4$: C, 41.66; H, 6.99; N, 29.15%. Yields were generally 30—60% by 0.02—0.1 mole scale preparation for all the ligands.

Apart from isolation and purification procedures, potassium salts of the alkylenebis(biuretato)cobaltate(III) complexes were prepared in a similar method as that employed for the preparation of potassium ethylenebis(biuretato)cobaltate(III).[4] In some cases active charcoal seems effective in complex formation. All the four complexes newly prepared were reprecipitated from aqueous solutions, whereas the known analogous complexes may be purified, if possible, only with organic solvents. Found for K[Co(*R*,*S*)-

bbpn]·H_2O: C, 23.49; H, 3.40; N, 23.43% and for the (*R*)-bbpn analog: C, 23.37; H, 3.39; N, 23.34%. Calcd for $C_7H_{12}N_6O_5CoK$: C, 23.47; H, 3.38; N, 23.46%. Found for K[Co(bbibn)]·H_2O: C, 25.89; H, 3.85; N, 22.21%. Calcd for $C_8H_{14}N_6O_5CoK$: C, 25.81; H, 3.79; N, 22.58%. Found for K[Co(*cis*-bbchxn)]·$0.5H_2O$: C, 30.56; H, 3.81; N, 21.02%. Calcd for $C_{10}H_{15}N_6O_{4.5}CoK$: C, 30.85; H, 3.88; N, 21.59%. Found for K[Co(bbtmen)]·$1.5H_2O$: C, 29.16; H, 4.57; N, 19.49%. Calcd for $C_{10}H_{19}N_6O_{5.5}CoK$: C, 29.34; H, 4.68; N, 20.53%. Yields were roughly 50, 45, 20, and 10%, respectively. The two known complexes were prepared according to the literature.[4] Found for K[Co(bbphen)]·H_2O: C, 30.69; H, 2.54; N, 20.95%. Calcd for $C_{10}H_{10}N_6O_5CoK$: C, 30.62; H, 2.57; N, 21.42%. Found for K[Co(bi)$_2$]·$0.5H_2O$: C, 15.78; H, 2.42; N, 27.30%. Calcd for $C_4H_7N_6O_{4.5}CoK$: C, 15.54; H, 2.28; N, 27.18%.

Measurements. The visible and ultraviolet absorption and reflectance spectra were recorded by a Hitachi 330 spectrophotometer. The CD and magnetic circular dichroism (MCD) spectra were obtained by a JASCO MOE-1 and a JASCO J-500C spectropolarimeter equipped with a 1.5-T electromagnet.

The low-temperature absorption spectra were measured with a hand-made cell and a glass Dewar provided with a light path. Body of the cell was made of a sheet of aluminum plate, on which polyacrylonitrile windows were mounted. Temperature measurements were carried out with a copper-constantan thermocouple dipped into sample solutions. With those samples that were employed for the low-temperature measurements, ambient-temperature measurements were also made for comparison.

Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer. Exciting lines were provided by a Spectra-Physics Model 164 Ar^+ ion laser (514.5, 501.7, 496.5, 488.0, 476.5, 472.7, 465.8, and 457.9 nm) and by a Coherent Radiation Model 599 dye laser employing Rhodamine 6G (588.0 and 567.8 nm). A rotating sample technique was used to minimize thermal decomposition of the sample by laser illumination. Samples were provided by K_2SO_4 disks. Intensities were measured with respect to the 981 cm^{-1} band of K_2SO_4 as internal standard and corrected for instrumental spectral response and the ν^4 law.

Theoretical

Molecular Orbitals. The extended Hückel (EH) molecular orbital calculations with self-consistent charge were carried out on bis(biuretato)cobaltate(III) and three related complex anions: bis(biuretato)-cuprate(II) and -nickelate(II), and tris(biuretato)-cobaltate(III).[6,7] The atomic coordinates from X-ray analyses[3,8] were adapted to fit D_{2h} or D_3 symmetry. The molecular coordinate system adopted is shown in Scheme 2. Double-ζ functions of Richardson et al. for +1 ions were used for metal 3d atomic orbitals (AO),[9] and single-ζ functions of Summerville and Hoffmann for all the other valence AO's including metal 4s and 4p.[10]

Valence orbital ionization potentials (3d-VOIP's) for $d^{n-1}s$ configurations[6b,11] were modified as below to give those results that enable a systematic explanation for the electronic spectra of the above four complexes. First, energy calculations were made for the copper(II) complex using modified A and B values (A' and B') and the original C, where $A'=\eta A$, $B'=\eta B$ (η is a scaling factor), and symbols A, B, and C have the usual significance.[6b] A reasonable result was obtained at $\eta=0.4$.[12] Parameters A' and B' for cobalt or nickel were determined by $A'_M=A_M-0.6A_{Cu}$ and $B'_M=B_M-0.6B_{Cu}$ (M=Co or Ni); i.e., the same amount as in copper was subtracted from the relevant original value regarding each parameter, A or B. The original values of A, B, and C of $d^{n-1}s$ and $d^{n-1}p$ configurations were used for metal 4s and 4p H_{ii}'s, respectively. Constant Coulomb integrals[10] were employed for hydrogen 1s and second-row-atom 2s and 2p orbitals. The present parametrization may be partly rationalized by intramolecular Madelung energies.[13] Wolfsberg–Helmholz approximation was employed for off-diagonal H_{ij}'s; the value of the interaction constant k was 1.75 unless otherwise stated. Open shell configuration with two singly-occupied orbitals was assumed for bis(biuretato)-cobaltate(III) anion.

Figure 1 displays the resulting energy levels for the molecular orbitals (MO) which are largely metal d or ligand π in character. Several MO's of largely oxygen σ were neglected from Fig. 1 for simplicity, though turned out to be located at ca. -112×10^3 cm^{-1} or lower wavenumbers in all the complexes. The present calculation for bis(biuretato)cobaltate(III) ion gave the ground state with $(yz)^1(zx)^1$ configuration in contrast with $(zx)^1(x^2-y^2)^1$ given by Birker et al.,[4] where (*yz*), (*zx*), etc. denote the MO's of largely d_{yz}, d_{zx}, etc.

Faraday Parameters for Charge Transfer Transitions. For $^3B_{1g}$ ground state with $(yz)^1(zx)^1$ configuration, such charge-transfer (CT) transitions as shown in Table 1 may be allowed between metal d and ligand π

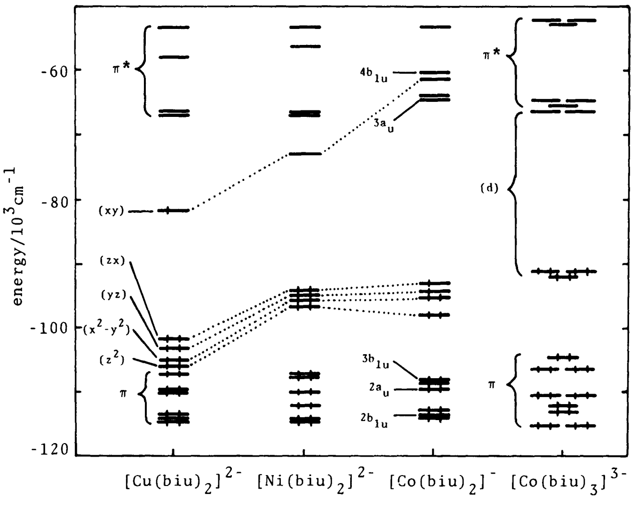


Fig. 1. Molecuar orbital energy diagram of bis(biuretato)cobaltate(III) and related complexes. Molecular orbitals of largely ligand σ are omitted.

Table 1. Possible Types of Charge-Transfer Transitions in $[\mathrm{Co(bi)_2}]^-$ for $^3\mathrm{B}_{1g}$ Ground State with $(yz)^1(zx)^1$ Configuration[a]

Excited states	LMCT	Abbrev.	MLCT	Abbrev.
$^3\mathrm{B}_{3u}$	$\mathrm{b}_{1u}(\pi_L) \rightarrow (yz)$	J_1	$(yz) \rightarrow \mathrm{b}_{1u}(\pi^*_L)$	J_1'
$^3\mathrm{B}_{2u}$	$\mathrm{b}_{1u}(\pi_L) \rightarrow (zx)$	J_2	$(zx) \rightarrow \mathrm{b}_{1u}(\pi^*_L)$	J_2'
$^3\mathrm{B}_{2u}$	$\mathrm{a}_u(\pi_L) \rightarrow (yz)$	J_3	$(yz) \rightarrow \mathrm{a}_u(\pi^*_L)$	J_3'
$^3\mathrm{B}_{3u}$	$\mathrm{a}_u(\pi_L) \rightarrow (zx)$	J_4	$(zx) \rightarrow \mathrm{a}_u(\pi^*_L)$	J_4'
$^3\mathrm{A}_u$	$\mathrm{a}_u(\pi_L) \rightarrow (xy)$	J_5	$(z^2) \rightarrow \mathrm{b}_{1u}(\pi^*_L)$	J_5'
$^3\mathrm{A}_u$	——	—	$(x^2-y^2) \rightarrow \mathrm{b}_{1u}(\pi^*_L)$	J_6'

a) For example, the abbreviation of ligand MO $\mathrm{b}_{1u}(\pi_L)$ represents the $n\mathrm{b}_{1u}(\pi_L)$ with n=1, 2, or 3, so J_1 the transition from one of the three MO's.

MO's in bis(biuretato)cobaltate(III) anion. Faraday parameters $\overline{B}_0$ for all the CT transitions can be formulated, as given below, in terms of the MO coefficients and the matrix elements of operator ∇ by the standard procedure:[14]

$$\overline{B}_0(J_1) = -\overline{B}_0(J_1') = -C(M_1/E_{3b})[M_3/(E_{32}E_{2b}) - \sqrt{3}M_4/(E_{31}E_{1b}) - M_2/(E_{43}E_{4b})], \tag{1}$$

$$\overline{B}_0(J_2) = -\overline{B}_0(J_2') = -C(M_2/E_{4b})[M_3/(E_{42}E_{2b}) + \sqrt{3}M_4/(E_{41}E_{1b}) + M_1/(E_{43}E_{3b})], \tag{2}$$

$$\overline{B}_0(J_3) = -\overline{B}_0(J_4) = C(M_5)^2/(E_{4a}E_{43}E_{3a}), \tag{3}$$

$$\overline{B}_0(J_5) = 2C(M_5M_6/E_{5a})[1/(E_{54}E_{4a}) + 1/(E_{53}E_{3a})], \tag{4}$$

$$\overline{B}_0(J_3') = -\overline{B}_0(J_3) + CM_5M_6/(E_{5a}E_{53}E_{3a}), \tag{5}$$

$$\overline{B}_0(J_4') = -\overline{B}_0(J_4) + CM_5M_6/(E_{5a}E_{54}E_{4a}), \tag{6}$$

$$\overline{B}_0(J_5') = \overline{B}_0(J_6') = 0, \tag{7}$$

where $\overline{B}_0(J)$ refers to a transition J given in Table 1; constant C is equal to 207.35 if MO energy differences E_{ij} are given in $10^3\,\mathrm{cm}^{-1}$ and quantities M_k in atomic unit; E_{ij} is defined by $E_i - E_j$; and the i or j values, a, b, and 1—5, denote the MO's, $n\mathrm{a}_u(\pi_L)$, $n\mathrm{b}_{1u}(\pi_L)$ (n: ordinal number), $9\mathrm{a}_g=(z^2)$, $10\mathrm{a}_g=(x^2-y^2)$, $3\mathrm{b}_{3g}=(yz)$, $4\mathrm{b}_{2g}=(zx)$, and $8\mathrm{b}_{1g}=(xy)$, respectively. Care must be taken especially in the MO symbols a and b, which indicate the π or π^* MO's relevant to the CT transition in question. Thus every equation connecting $\overline{B}_0(J_i)$ for a ligand-to-metal (LM) and $\overline{B}_0(J_i')$ for a metal-to-ligand (ML) CT transition in Eqs. 1, 2, 5, and 6 means only a formal resemblance between the two $\overline{B}_0$'s. In the above formulation, two-center magnetic-transition-moment integrals were ignored and the MO's of mainly metal d character were approximated by pure d orbitals.

The quantities, M_k, can be expressed as:

$$M_1 = -4\sum_{m=1}^{3} c_{bm}[\cos^2\theta_m <ZX|\nabla_X|Z>^m + \sin^2\theta_m <YZ|\nabla_Y|Z>^m] - 2c_{b4}<ZX|\nabla_X|Z>^4, \tag{8}$$

$$M_2 = 4\sum_{m=1}^{3} c_{bm}[\sin^2\theta_m <ZX|\nabla_X|Z>^m + \cos^2\theta_m <YZ|\nabla_Y|Z>^m] + 2c_{b4}<YZ|\nabla_Y|Z>^4, \tag{9}$$

$$M_3 = -4\sum_{m=1}^{3} c_{bm}\cos(2\theta_m)<X^2 - Y^2|\nabla_Z|Z>^m - 2c_{b4}<X^2 - Y^2|\nabla_Z|Z>^4, \tag{10}$$

$$M_4 = -4\sum_{m=1}^{3} c_{bm}<Z^2|\nabla_Z|Z>^m - 2c_{b4}<Z^2|\nabla_Z|Z>^4, \tag{11}$$

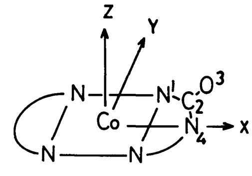
$$M_5 = -2\sum_{m=1}^{3} c_{am}\sin(2\theta_m)[<ZX|\nabla_X|Z>^m - <YZ|\nabla_Y|Z>^m], \tag{12}$$

$$M_6 = 4\sum_{m=1}^{3} c_{am}\sin(2\theta_m)<X^2 - Y^2|\nabla_Z|Z>^m, \tag{13}$$

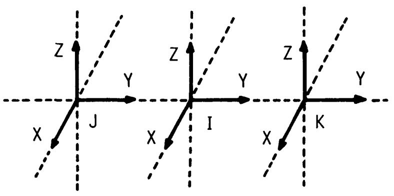
where c_{im} is the amplitude coefficient of $2\mathrm{p}_\pi$ AO on atom m in the relevant π-MO i [i=a or b for a_u or b_{1u}; and m=1—4 for N(terminal), C, O, and N(central) atom, respectively, of the N-CO-N group in the first quadrant of the molecular coordinate system (Scheme 2)]. The acute angle θ_m is defined by the x-axis and the position vector of atom m. Two-center integrals $<J|\nabla_I|K>^m$, referring to metal $3\mathrm{d}_J$ and atom-m $2\mathrm{p}_K$ AO's, were defined relative to the local coordinate system shown in Scheme 3 and evaluated by Kral's formulas.[15] Thus M_k's can be written by

$$M_k = \sum_{m=1}^{4} c_{im}C_{km}, \tag{14}$$

where C_{km}'s, which were evaluated as given in Table 2,



Scheme 2.



Scheme 3.

Table 2. C_{km} Values for $[Co(bi)_2]^-$

k	C_{k1}	C_{k2}	C_{k3}	C_{k4}
1	0.339	0.025	0.00055	0.0010
2	−0.339	−0.070	−0.00102	−0.0092
3	0.0	0.030	0.00028	0.0051
4	0.358	0.042	0.00058	0.0041
5	−0.198	−0.027	−0.00063	0.0
6	−0.339	−0.037	−0.00073	0.0

are dependent only on the given AO set and the molecular geometry.

The above formulation of $\bar{B}_0$ reflects mainly symmetry properties of the system, so it may be applicable to other d^6 planar complexes with a slight modification in M_k's, or Eqs. 8—13. In addition, Eqs. 1—7 need not be revised by a change in the energy order of MO's so long as it takes place within any of the doubly-occupied, the singly-occupied, and the vacant MO's.

The numerical results of $\bar{B}_0$ for several low-energy CT transitions are exemplified together with the calculated dipole strengths $\bar{D}_0$ in Table 3.

Results and Discussion

The absorption, CD, and MCD data obtained in DMSO and in aqueous solution at ambient temperature are shown in Tables 4 and 5 and Figs. 2—5. Abbreviations for intense bands, I—IV, were also denoted in Fig. 2. Spectral features in methanol solution were of intermediate between those in DMSO and aqueous solutions, although related data are not given.

Assignment of the Absorption Bands. An Intense Band at ca. 20×10^3 cm^{-1}: The bis(biuretato)cobaltate(III)-type complexes generally showed an intense absorption band ($\varepsilon \simeq 7000$ in DMSO) at ca. 20×10^3 cm^{-1}. This band (band I) may be attributed to CT transitions between metal d and ligand π MO's because of the high intensities and of the relatively low energies. Numerical data of band I have once been given but not discussed at all.[3] From the absorption-band shape and the dispersion pattern of negative A-term type in this region, band I consists of at least two nearly degenerate components.

The band I for the complexes of bis(biuretato)-cobaltate(III) type was observed at much lower energies than the lowest-lying intense bands for the three related complexes.[16] The relative order of the transition energies is in agreement with the EH energy diagrams (Fig. 1) if band I is assigned to the lowest-lying LMCT transitions, whereas a different situation would be expected if it is assigned to MLCT.

Figure 6 shows the Raman spectrum (514.5 nm excitation) of the mother complex, $K[Co(bi)_2]\cdot 0.5H_2O$, of the alkylenebis(biuretato) complexes discussed above. Assignment of the observed Raman bands was made based on a close correlation between the peaks in the Raman spectra of $K[Co(bi)_2]\cdot 0.5H_2O$ and of $K_2[Cu(bi)_2]$[17] and summarized in Table 6.

It is well known that resonance Raman effects reflect the nature of the resonant electronic transition; that is, if a Raman band showed a strong resonance enhancement near the frequency of an electronic excitation within a certain chromophore, the equilibrium conformation of the chromophore should be considered to be distorted along the normal coordinate for the Raman band.[18] Figure 7 shows the excitation profiles of the Raman bands for which strong enhancements were observed on resonance with band I. Taking the

Table 3. The Values of $\bar{B}_0$ and $\bar{D}_0$ Parameters and Transition Energies Calculated by the EHMO Method[a)] for Several Low-Energy CT Transitions in $[Co(bi)_2]^-$ with $^3B_{1g}$ Ground State

LMCT transition				
π-MO	Transition	Energy	$\bar{B}_0$	$\bar{D}_0$
		10^3 cm^{-1}	10^{-3} D^2 cm	D^2
$3b_{1u}$	J_1	13.8; 17.1	−0.43; 0.37	5.8; 3.0
$3b_{1u}$	J_2	15.0; 18.9	13.6; 4.6	4.4; 2.1
$2a_u$	J_3	15.4; 18.1	5.3; 2.3	3.3; 2.2
$2a_u$	J_4	16.6; 19.9	−5.3; −2.3	2.9; 1.8
$2b_{1u}$	J_1	19.8; 23.2	−1.3; −0.34	2.4; 1.8
$2b_{1u}$	J_2	20.9; 25.0	6.5; 3.3	2.4; 1.7
MLCT transition				
π-MO	Transition	Energy	$\bar{B}_0$	$\bar{D}_0$
		10^3 cm^{-1}	10^{-3} D^2 cm	D^2
$3a_u$	J_4'	28.4; 36.1	0.12; 0.23	0.20; 0.14
$3a_u$	J_3'	29.5; 37.9	−0.52; −0.07	0.18; 0.12
$4b_{1u}$	J_2'	32.5; 36.3	−0.011; −0.13	0.02; 0.10
$4b_{1u}$	J_1'	33.7; 38.1	−0.004; 0.06	0.0001; 0.05

a) Two set of the Wolfsberg-Helmholz constants were tested: $k_\sigma = k_\pi = 1.75$, and $K_\sigma = 1.75$ and $k_\pi = 2.00$. The results obtained by the former and the latter set are given on the left and right of semicolon, respectively.

Table 4. Absorption Data of the Complexes[a]

Complex	Solvent[b]	$\tilde{\nu}_{max}/10^3$ cm^{-1} (log(ε/mol^{-1} dm^3 cm^{-1}))		
K[Co((*R*,*S*)-bbpn)]·H_2O	D	11.4sh(1.8)	13.04(2.13)	18.83(3.85)
		24.3sh(3.5)	28.17(3.55)	36.66(3.79)
	W	11.21(1.35)	13.09(1.83)	20.41(3.55)
		23.8sh(3.5)	37.7sh(3.7)	
K[Co(bbibn)]·H_2O	D	11.4sh(1.8)	12.1sh(1.9)	12.82(2.16)
		18.87(3.87)	24.2sh(3.5)	28.17(3.54)
		35.84(3.78)		
	W	11.56(1.52)	12.3sh(1.9)	12.82(1.96)
		20.37(3.61)	23.8sh(3.5)	37.7sh(3.8)
K[Co(*cis*-bbchxn)]·$0.5H_2O$	D	≈11sh(1.7)	12.0sh(2.1)	12.76(2.72)
		18.90(3.87)	23.36(3.55)	27.93(3.59)
		35.59(3.83)		
	W	10.5sh(1.5)	12.3sh(2.0)	12.66(2.02)
		20.53(3.50)	22.9sh(3.4)	36.5sh(3.8)
K[Co(bbtmen)]·$1.5H_2O$	D	≈11sh(1.7)	12.0sh(2.0)	12.74(2.18)
		19.08(3.86)	23.53(3.51)	28.2sh(3.6)
		34.84(3.78)		
	W	11.3sh(1.7)	12.3sh(2.1)	12.72(2.14)
		20.70(3.65)	23.3sh(3.6)	36.50(3.76)
K[Co(bbphen)]·H_2O	D	11.17(3.03)	13.80(3.19)	19.19(3.83)
		26.8sh(3.5)	27.88(3.57)	31.0sh(3.7)
		34.1sh(4.0)		
	W	15.2sh(2.0)	22.54(2.69)	27.2sh(2.8)
		≈36br(4.22)		

a) sh denotes shoulder and br broad band. b) D and W denote DMF and water, respectively.

Table 5. MCD and CD Data of the Complexes

Complex	Solvent[a]	$\tilde{\nu}_{ext}/10^3$ cm^{-1} ($\Delta\varepsilon_M$/mol^{-1} dm^3 cm^{-1} T^{-1})		
K[Co((*R*,*S*)-bbpn)]·H_2O	D	12.18(0.006)	13.00(−0.04)	18.20(6.75)
		20.30(−5.58)	27.07(−1.59)	33.57(0.17)
	W	13.02(−0.04)	18.41(1.10)	21.90(−1.25)
		29.20(−0.50)	39.95(−0.28)	
K[Co((*R*)-bbpn)]·H_2O[b]	D	11.03(−0.72)	13.19(−1.81)	18.32(8.45)
		21.98(−1.07)	24.39(3.15)	30.40(−1.45)
	W	10.71(−0.51)	13.09(−1.25)	18.83(2.34)
		26.39(1.75)	30.96(−0.69)	
K[Co(bbibn)]·H_2O	D	11.42(−0.03)	12.90(−0.09)	18.24(6.99)
		20.31(−5.61)	26.78(−1.48)	33.31(0.27)
	W	12.92(−0.05)	18.42(1.14)	21.83(−1.43)
		28.92(−0.65)	39.60(−0.25)	
K[Co(*cis*-bbchxn)]·$0.5H_2O$	D	12.85(−0.11)	17.96(6.12)	20.19(−4.53)
		26.66(−1.36)		
	W	12.84(−0.08)	17.80(1.75)	21.45(−1.95)
		28.95(−0.99)	38.88(−0.35)	
K[Co(bbtmen)]·$1.5H_2O$	D	11.69(−0.10)	12.81(−0.15)	18.27(6.54)
		20.42(−4.93)	26.76(−1.53)	34.05(0.02)
		37.31(−0.29)		
	W	11.30(−0.04)	12.78(−0.29)	18.30(2.05)
		21.79(−2.39)	29.12(−1.13)	39.57(−0.20)
K[Co(bbphen)]·H_2O	D	10.08(−0.50)	12.76(−0.47)	14.30(0.22)
		18.23(5.00)	20.49(−3.49)	25.55(−1.84)
		31.03(0.12)		

a) See footnote b) in Table 1. b) For this complex, $\Delta\varepsilon_M$ is read as $\Delta\varepsilon$.

intensity of each band to be unity at 588.0 nm, the intensities of the bands at 392 and 815 cm^{-1} became ca. 30, those at 548, 1013, and 1625 cm^{-1} ca. 15, and those at 273 and 1362 cm^{-1} ca. 10, at the maximum of band I. The Raman bands arise from the skeletal stretching and deformation vibrations of the chelate ring as shown in Table 6. This observation indicates that the electron which is participating in the transitions of band I should be extensively delocalized over the ligand, being consistent with the assignment given above for band I.

As mentioned before, a marked MCD generally

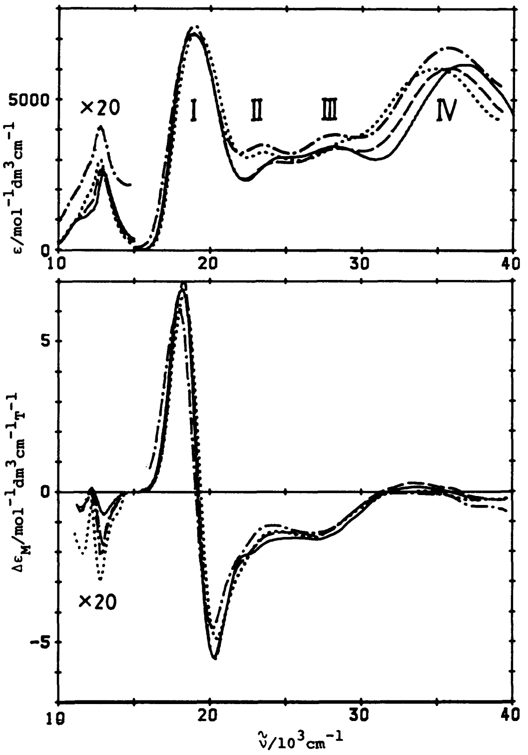


Fig. 2. Absorption and MCD spectra in DMSO solutions: K[Co((*R*,*S*)-bbpn)] (——), K[Co(bbibn)] (----), K[Co(*cis*-bbchxn)] (—·—·—), and K[Co(bbtmen)] (········).

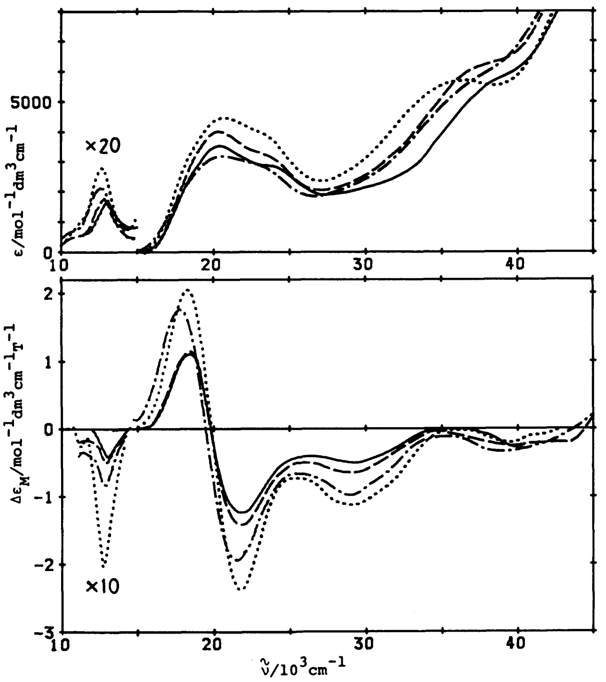


Fig. 3. Absorption and MCD spectra in aqueous solutions: K[Co((*R*,*S*)-bbpn)] (——), K[Co(bbibn)] (----), K[Co(*cis*-bbchxn)] (—·—·—), and K[Co(bbtmen)] (········).

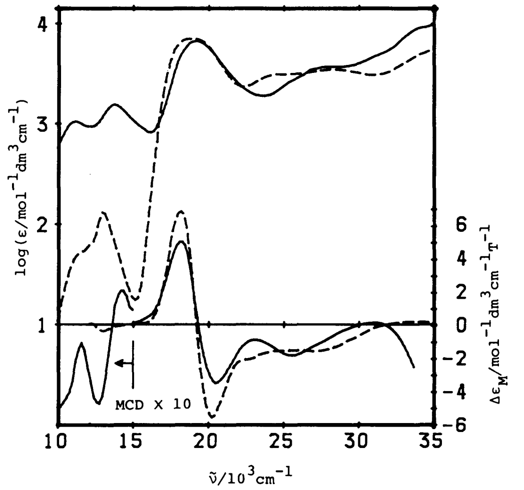


Fig. 4. Absorption and MCD spectra of K[Co(bbphen)] in DMSO solution (——). The spectra of K[Co((*R*,*S*)-bbpn)] (----) are added for comparison.

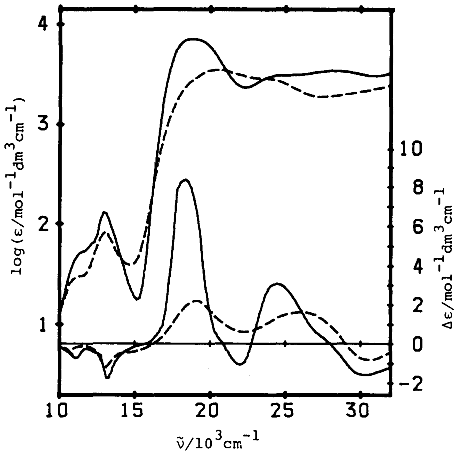


Fig. 5. Absorption and CD spectra of K[Co((*R*)-bbpn)] in DMSO (——) and in aqueous solution (----). The absorption spectra are added for comparison.

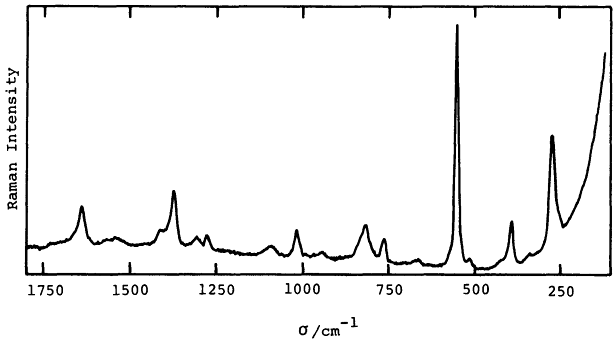


Fig. 6. Raman spectrum of K[Co(bi)$_2$]·0.5H$_2$O (514.5 nm excitation).

appears in the region of band I. Its negative *A*-term pattern is retained among all the planar cobalt(III) complexes investigated. In Eqs. 1—3, so-called pseudo-*A* terms are found as couples of the *B* terms, i.e., of $\bar{B}_0(J_3)$ and $\bar{B}_0(J_4)$ and of the third terms in both $\bar{B}_0(J_1)$ and $\bar{B}_0(J_2)$, where each couple refers to a common ligand MO of a_u or b_{1u} symmetry. Such a couple of the *B* terms can be correlated by the following relation to the *A* term of a degenerate CT transition in square-planar model complex $[Co(NH_2)_4]^-$ with D_{4h} symmetry:

$$\bar{A}_1(J) = -\bar{B}_0(J')\Delta W = \bar{B}_0(J'')\Delta W, \tag{15}$$

where $\bar{A}_1(J)$ is the Faraday parameter defined for a degenerate transition J, J′ and J″ are the lower and the higher split components in the lower symmetry, and ΔW is the splitting between J′ and J″.[14a)] For example, if transitions J_1 and J_2 are chosen as J′ and J″ and the energy difference $\Delta W = E_{43}$ is brought close to zero, the contributions from the first and the second terms of the right-hand sides of Eqs. 1 and 2 become negligible and Eq. 15 comes to hold exactly for J=an $a_{2u}(\pi_L)$-to-$e_g(d_{yz,zx})$ transition. If our $[Co(bi)_2]^-$ model is supposed to be very close to D_{4h}, only the first term $c_{i1}C_{k1}$ must survive in Eq. 14 as inferred from Table 2. Thus the influence of the non-ligating atoms on ligand π MO's disappears. Therefore the pseudo-*A* terms in the bis(biuretato) complexes can be discussed in terms of the square-planar model complex.

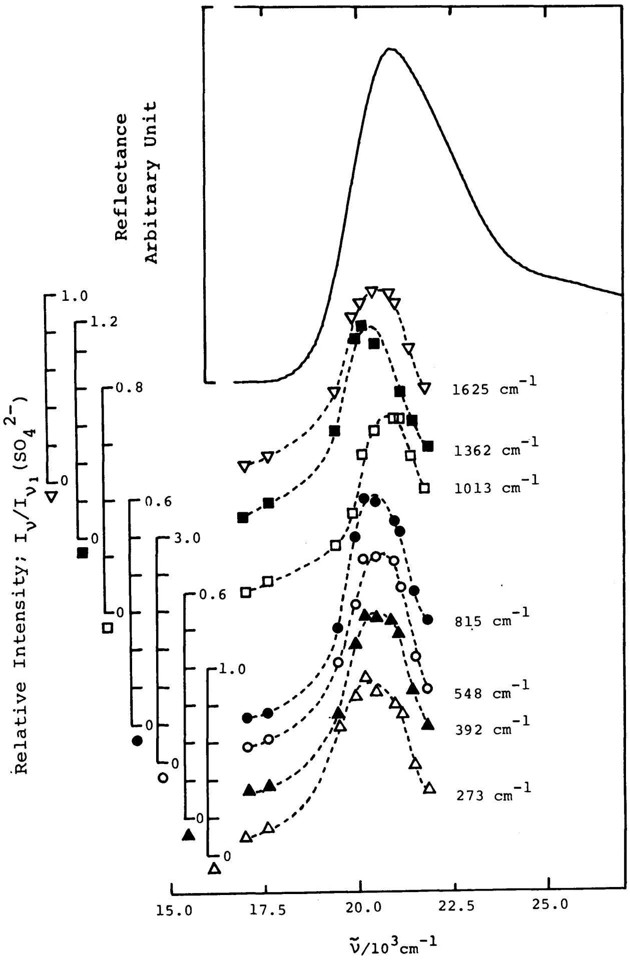


Fig. 7. Excitation profiles of the Raman bands of $K[Co(bi)_2]\cdot 0.5H_2O$ (----) together with the diffuse reflectance spectrum (——).

For the *A* terms of the latter model complex, the following relations are easily shown to hold:

$$\bar{A}_1/\bar{D}_0 = 1 \text{ for transitions between } e_g(d_{yz,zx}) \text{ and } a_{2u}(\pi_L), \tag{16}$$

$$\bar{A}_1/\bar{D}_0 = -1 \text{ for those between } e_g(d_{yz,zx}) \text{ and } b_{1u}(\pi_L), \tag{17}$$

where $\bar{D}_0$ are defined according to the literature.[14a)] In addition, Eqs. 16 and 17 hold for various assumed ground states of $^3A_{2g}$ or ^3E_g. It should be noted that the a_{2u} and the b_{1u} MO's of largely ligand π in the square-planar complex correspond to a b_{1u} and an a_u MO's in the D_{2h} complex, respectively. Furthermore, the $^3A_{2g}(D_{4h})$ ground state corresponds to the $^3B_{1g}(D_{2h})$ with $(yz)^1(zx)^1$ configuration, whereas the $^3B_{2g}(D_{2h})$ ground state with $(x^2-y^2)^1(zx)^1$ is considerably different from every state of the D_{4h} model complex, because it has different occupation numbers, i.e., 2 and 1, for (*yz*) and (*zx*).

The Gaussian curve fittings were carried out for the band I region of the observed absorption and MCD spectra of the bbpn complex in DMSO (Fig. 8).[19)] The $\bar{B}_0$ and $\bar{D}_0$ values were determined as given in Table 7. The $\bar{A}_1/\bar{D}_0$ value was also estimated at ca. −1.5 by use of Eq. 15 and the data in Table 7. By comparison of these results with the calculated values in Table 3 and with

Table 6. Observed Raman Frequencies (cm^{-1}) and Their Assignments for $K[Co(bi)_2]\cdot 0.5H_2O$

Obsd.	Assignment	Obsd.	Assignment
1625*	ν(C=O)+ν(C-N)	1013*	ν(C-N)
1530	ν(C-N)+δ(C=O)	815*	ring def.
1400	ν(C-N)+δ(C=O)	763	δ(C=O)+ν(Co-N)
1362*	ν(C=O)+δ(N-H)	548*	ring def.+δ(C=O)+ν(Co-N)
1305	δ(N-H)	509	ring def.+δ(C=O)
1267	δ(N-H)	392*	ν(Co-N)+(C=O)+ring def.
1094	ν(C-N)	273*	ν(Co-N)

* Bands of which excitation profiles were obtained.

Table 7. The Curve Analysis Results for the Two Components of Band I of K[Co((*R,S*)-bbpn)] in DMSO[a]

$\tilde{\nu}_{ext}$	δ[b]	$(\varepsilon/\tilde{\nu})_{ext}$	$(\Delta\varepsilon_M/\tilde{\nu})_{ext}$	$\bar{D}_0$	$\bar{B}_0$
$10^3\,cm^{-1}$	$10^3\,cm^{-1}$	$mol^{-1}\,dm^3$	$10^{-3}\,mol^{-1}\,dm^3\,T^{-1}$	D^2	$10^{-3}\,D^2\,cm$
18.19	1.81	0.300	0.136	1.76	1.72
19.87	2.07	0.250	−0.098	1.69	−1.42

a) Details of the method are given in text and in Ref. 19. b) The whole width at half height.

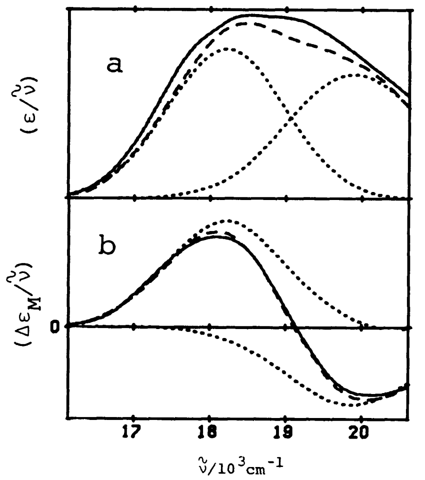


Fig. 8. Gaussian fittings of a) absorption and b) MCD spectra in the region of band I of K[Co(bbpn)] in DMSO: observed (——), calculated (----), and component curves (--------).

Eq. 17, band I may be assigned to the LMCT transitions of $a_u(\pi_L)$ to (yz) and (zx), that is, J_3 and J_4, which are derived from a b_{1u}-to-$e_g(yz,zx)$ transition in $[Co(NH_2)_4]^-$. Such a producibility of dispersion pattern in CT transitions is not specific for the $(yz)^1(zx)^1$ but in common with the $(yz,zx)^3(i)^1$ configuration, where $i=x^2-y^2$ or z^2. It should be noted in this context, however, that the energy difference of (yz) and (zx), ΔW, should be small enough only in the latter configuration, so as to secure essentially equal electron population on themselves, or to make the Boltzmann factor $\exp(-\Delta W/kT)$ unity. The situation is unlikely as in the $(zx)^1(x^2-y^2)^1$ configuration cited before.[4]

Regarding the transition energies, however, the above band assignment is less satisfactory because in our EHMO results (Fig. 1) $3b_{1u}(\pi_L)$ lies above $2a_u(\pi_L)$ even though the energy difference is small. This point will be mentioned again in the next subsection.

Other Intense Bands: Three other intense absorption bands were generally observed at 23—24 (band II), 27—29 (band III), and ca. $35\times10^3\,cm^{-1}$ (band IV). Although many d-d bands are expected besides LMCT and MLCT bands throughout the wavenumber region, most of the absorption intensities may also be attributed to CT transitions from their high intensities.

Unfortunately, our EHMO calculations could not reproduce the transition energies and MCD intensities of bands I—IV simultaneously; the order of MO energies for k=1.75 (Fig. 1) was not altered by various k values except for the energy of (xy),[20] and the amplitude coefficients in each MO and the calculated B terms for each CT transition (Table 3) were rather slightly dependent on k. Although any clear-cut assignment of bands II—IV cannot be made in these circumstances, it is supposed that the signs of B terms are usable as the basis for the following discussion but the transition energies are unusable since the difficulty in quantitative determination by MO method is well known.[21]

Roughly speaking, the MCD of the bands decreases in intensity with increase in transition energies, i.e., in the order of I—IV, in line with the assignment of all these bands to CT and Eqs. 1—6. Since the MO results and Eqs. 1 and 2 predicted a net positive B term for the lowest-lying LMCT of (J_1, J_2) and a net negative one for the lowest-lying MLCT of (J_1', J_2') as seen in Table 3, bands IV and III may be tentatively assigned to the LMCT and the MLCT, respectively. Since band II seemingly resembles band III in the absorption spectra, MLCT may also be assigned to band II. The g value for a relatively strong CD accompanied by band II in the (*R*)-bbpn complex was one to two orders of magnitude too low for the band to be regarded as magnetically allowed. Since band II of the (*R,S*)-bbpn complex lost a significant amount of the intensity at liquid nitrogen temperature (Fig. 9b), some d-d character may also be suggested for band II.

Also in the region of bands II—IV the bbphen complex showed a spectral behavior slightly different from that in the other complexes.

Weak Bands in 10—16×10³ cm⁻¹ Region: The complexes of bis(biuretato)cobaltate(III)-type generally exhibited a group of weak absorption bands in this region in both DMSO and aqueous solutions. Two bands were always clearly observed at ca. 11 and $13\times10^3\,cm^{-1}$ and occasionally accompanied by a fine structure consisting of one to several very weak bands. In the region, our data in DMSO solutions nearly reproduced those for the analogous complexes reported by Birker et al.[4] According to the latter authors the absorption bands measured both in DMSO and in ethanol solution as well as in the solid state of

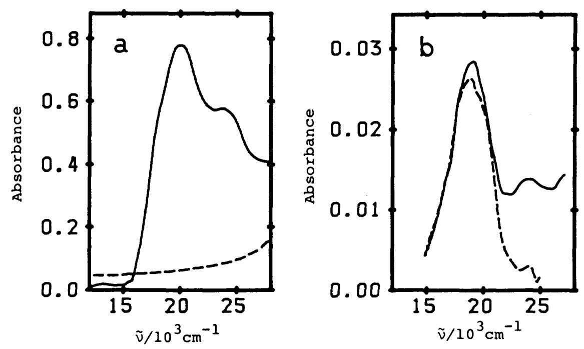


Fig. 9. Absorption spectra of K[Co((*R*,*S*)-bbpn)] at ambient temperature (——) and at 77 K (----): a) in water-glycerol (1/1 volume ratio), and b) in DMF-chloroform (1/1 volume ratio).

potassium bis(3-propylbiuretato)cobaltate(III) were quite the same; so the solvent molecules are not likely to interact with the planar $Co(N)_4$ species. It may be also the case with the complexes investigated in the present work as assumed in the preceding discussion.

The bands under discussion can be assigned to d-d transitions because of the low intensities. Furthermore, the *g* value, $|\Delta\varepsilon|/\varepsilon$, for the (*R*)-bbpn complex was roughly 1×10^{-2} in the region, indicating that the bands are magnetically allowed in agreement with the above assignment. Bour et al. assigned the 11 and $13\times10^3\,cm^{-1}$ bands to the transitions ${}^3B_{2g}\rightarrow{}^3A_{2g}$ and ${}^3B_{2g}\rightarrow{}^3E_g$, respectively.[2] This assignment, however, seems to assume an orbital energy too high for (z^2). As seen in Fig. 1, (z^2) may be lowered close to a level of (x^2—y^2), (yz), and (zx) by a configuration interaction involving metal 4s-orbital. Half-value widths of the two main bands are only 1.2—$1.6\times10^3\,cm^{-1}$, being considerably narrower than those observed for the spin allowed bands due to transitions from nearly nonbonding d-orbitals[22] to strongly antibonding d_{xy} orbital; e.g., the band widths of planar bis(aminocarboxamidato)-nickel(II) complexes amount to $2.3\times10^3\,cm^{-1}$ or larger.[23] Therefore the weak bands in question would be more appropriately assigned to some transitions among the nonbonding d-orbitals rather than nonbonding d to d_{xy}. The fine structure observed on the d-d bands may reasonably be attributed to some spin-forbidden d-d transitions as judged by an angular overlap model examination of d^6 system.[24]

In agreement with the above discussion, the d-d transitions to d_{xy} orbital are located at $15\times10^3\,cm^{-1}$ or higher wavenumbers even in square-planar cobalt(II) complexes.[25] Exceptionally high intensities of the two bands of the bbphen complex in DMSO (Fig. 4) have been discussed by the previous authors.[4]

Thermochromism. We found a marked thermochromism for the five bis(biuretato)cobaltate(III)-type complexes in water-glycerol (1/1 volume ratio); with the bbphen complex, a small amount of DMSO was added to effect the dissolution. Preliminary measurements were carried out for the absorption spectra of the complexes below ambient temperature. One of the results is shown in Fig. 9a. In general the red color reversibly faded to pale yellow or pale violet when the solutions were cooled to 77 K. The bbtmen complex showed a slightly less pronounced temperature-dependence; its color was changed to bright orange at 77 K.

On the contrary the five complexes did not show any pronounced color change in DMSO or DMF solution, i.e., in nonaqueous media; as an example the temperature dependence of a nonaqueous glassy solution is shown in Fig. 9b. Some, not all, of the solutions changed the colors when a considerable amount of water was added. Red color of those solutions which remarkably faded when cooled to 77 K was darkened when heated. Thus the thermochromism was observed in a rather wide range of temperature. As an example of the detailed behavior, we observed that the decoloration of the bbpn complex was accelerated under −20 °C in the water-glycerol mixture. A hyperchromic effect was also observed when organic solvents such as alcohols and DMSO were added to aqueous solutions. Thus the thermochromism seems to occur only in water-containing media. Seemingly no thermochromism could be detected about the solid samples, however, in agreement with the knowledge that the spin-triplet ground state is retained in potassium bis(3-propylbiuretato)cobaltate(III) dihydrate even at −250 °C;[4] interestingly this substance contains water of crystallization.

While absorption, CD, and MCD spectra of the bis(biuretato)-cobaltate(III)-type complexes were appreciably deformed in aqueous solution, characteristic features exhibitied in DMSO were still retained except for the bbphen complex (Figs. 2 and 3). Dependence of both absorption and MCD spectra upon modification of the ligands was observed more remarkably in aqueous solution than in DMSO. The less the number of out-of-plane substituents are on the bridging group R in Scheme 1, the larger the observed solvent effect became. This fact implies that steric interactions between the bridging groups and water molecules dominate the spectral behavior.

All the above observations may be explained if it is supposed that each complex exists as an equilibrium mixture of the four-coordinate square-planar species and one or more five- or six-coordinate species in aqueous solution, and that any one of the non-planar species comes to dominate with lowering of temperature. This explanation may not be unreasonable in view of the residual ability of coordination in the analogous complexes.[4] Irreversible decomposition of the five complexes containing the bbphen complex seems negligible from the time-dependence of the absorption spectra. The bbpn complex in aqueous solution, for example, varied less than 1% in absorb-

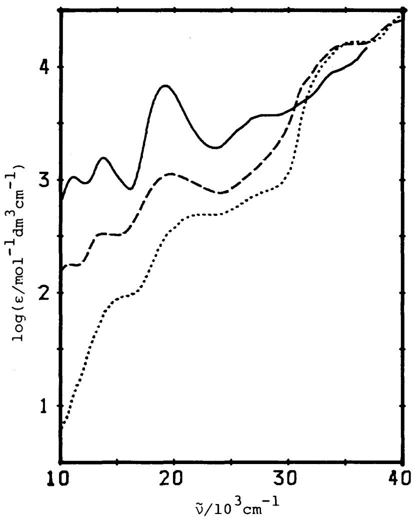


Fig. 10. Absorption spectra of K[Co(bbphen)]: in DMSO (——), in DMSO-water (1/1 volume ratio) (----), and in water (--------). The spectrum in DMSO solution is added for comparison.

ance for 8 h.

The absorption spectrum of the bbphen complex was deformed much more seriously than the other analogous complexes in aqueous solution, as shown in Fig. 10. The spectrum in the region of ca. 30×10^3 cm^{-1} or lower wavenumbers is seemingly dominated by ligand field transitions; accordingly a profound conversion of the planar species is likely to take place to give some usual low-spin cobalt(III) species. The spectral behavior of the bbphen complex should be considered, however, to be not so specific but rather general for all the five complexes since dark brown color of the bbphen complex in aqueous solution instantly turned to bright red, characteristic of the planar species, when a large amount of DMSO was added. Every absorption spectrum given in Fig. 10 obeys Beer's law almost exactly; it showed a negligible time-dependence for a few hours. The observations as a whole rule out the possibility that some associated species might play an important role in the temperature and solvent dependences of absorption spectra of the bis(biuretato)cobaltate(III)-type complexes.

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