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Article

Electronic Ground State and the d–d Transitions in Bis(biuretato)cobaltate(III) Ions

Sven E. Harnung*,† **and Erik Larsen**‡

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark, and Department of Natural Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg, Denmark

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The electronic structure of a class of compounds based on the bis(biuretato)cobaltate(III) ion has been investigated by spectroscopic methods (UV–vis, CD, MCD), magnetic susceptibility, and ligand field theory. The concept of *molecules in molecules* has been introduced to account for the conjugated π system of the whole ligand entity and its perturbation of the metal ion 3d orbitals. The Slater–Condon–Racah scheme was fully exploited; in particular, differences in occupation numbers of the spin orbitals have been used in the spectral assignments of the d–d transitions. The energy calculations used one σ parameter, two π parameters, and two Racah parameters. The π parameters, which were derived from Orgel orbitals of χ and ψ type, were found to be positive. The observed charge-transfer transitions are metal ← ligand. The results of our calculations are in agreement with available experimental data, including the spin triplet ground state and the position of the lower d–d transitions. The approach is general and, for example, applicable to heme iron(II).

Introduction

An important class of iron(II) and cobalt(III) complexes has a four-coordinate planar coordination geometry. This is quite unusual for metal ions with a $3d^6$ electron configuration which are most often octahedrally coordinated. It has proven surprisingly difficult to explain the electronic structure of such compounds, but in this paper, we present new experimental results and show how ligand-field theory leads to a consistent interpretation of the known data.

The unusual electronic properties of $3d^6$ systems were first discovered in the iron(II) complexes with phthalocyanines and porphyrins. After years of investigations, Klemm et al.[1] in 1939 determined the magnetic susceptibility of (phthalocyaninato)iron(II) to be $\mu_{\text{eff}} = 3.74$. This indicates that the electronic ground state is a spin triplet, usually called an "intermediate spin" because the value $S = 1$ lies "between" that of the singlet and quintet states. Dale et al. determined μ_{eff} to be 3.71 in 1968 and made a Mössbauer-effect study of this compound, but they were not able to deduce correctly the energetic sequence of the d-orbitals.[2]

In the seventies, two remarkable experimental works appeared. The first one by A. Thomson et al.[3] deduced, from the ligand ← metal charge transfer in MCD of (phthalocyaninato)iron(II), the sequence of the d-orbitals shown in our eq 1 below. The important issue is that the d_{z^2} orbital is double-occupied and lies energetically lower than the single-occupied d_{yz} and d_{zx} orbitals. In the second work, La Mar et al.[4] deduced the same sequence of d-orbitals from the ^{1}H NMR spectra of (porphyrinato)iron(II) through a series of very delicate arguments. It has been generally accepted that such planar four-coordinate species owed their existence to π-bonding and attempts have been made to include this in the ligand-field calculations. However, recent works have not concentrated on symmetry adaptation of ligand orbitals but have instead attempted to adapt the 3d-orbitals to the ligand π-orbitals.[5,6,7]

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* To whom correspondence should be addressed. E-mail: harnung@kiku.dk.

† Department of Chemistry.

‡ Department of Natural Sciences

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Much work has been concentrated on the explanation of the triplet ground state within accepted theoretical frameworks and with plausible parameters. A few papers have tried to include other data, in particular UV−vis absorption spectra, but the results have been meager.

A complete crystal-field computation on a $3d^6$ electron configuration assuming D_{4h} symmetry showed that a ${}^3A_{2g}$ ground state is possible but only for utterly unrealistic choices of the parameters *Dq*, *Ds*, and *Dt*.[8] This kind of calculations was later modified as shown in Table 3 but without a satisfactory result. In this connection, we note that the parameters *Ds* and *Dt* have no direct relation to the σ- and π-bonding properties and that square planar, four-coordination described by *Ds* and *Dt* requires a huge distortation of a six-coordinated octahedron, described by *Dq*.

Charge density studies on (phthalocyaninato)iron(II) and on (tetraphenylporphyrinato) iron(II) have been performed, and while the charge density of the former compound is in agreement with a ${}^3A_{2g}$ ground state (D_{4h}), the results are less clear for the latter one.[9]

In the present paper, we concentrate on cobalt(III) coordination compounds derived from bis(biuretato)cobaltate(III)(1−).[10] The ligands are entities where two biuret units have been bridged by one diamine, see **I**. The complexes are well defined anions, and in comparison with the iron(II) entities mentioned above, they are easy to study from a spectroscopic point of view. From a computational point of view, the four negative charges from the ligand apparently augment the likeliness for a planar four-coordinate structure, and the combined effect of the two planar π systems simplify the choice of ligand-field parameters. Our experimental studies can be rationalized if we assume that the ground state in D_{2h} symmetry is

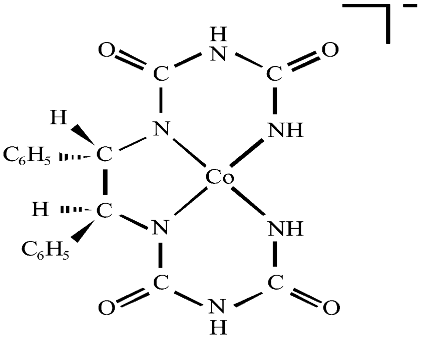
$$\xi\,(5\pi b_{3g})^2\,(5\pi b_{1u})^2\,(3d_{x^2-y^2})^2\,(3d_{z^2})^2\,(3d_{zx})^1\,(3d_{yz})^1\,(3d_{xy})^0;\quad {}^3B_{1g}\,(D_{2h}) \qquad (1)$$

using the coordinate system of **III**. Here, 5π denotes the ligand HOMO’s, the 3d’s are metal one-electron orbitals, and the symbol ξ embraces all the additional quantum numbers that are necessary for the full characterization of the state. The filled d_{z^2} orbital explains why two more ligators are not taken up by the metal ion.

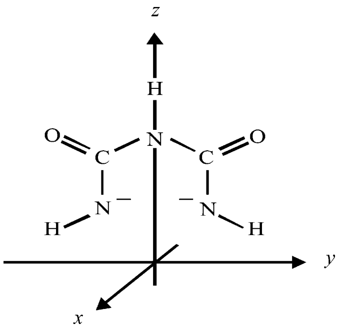
Experimental Section

Biuret is 1,3,5-triazapentane-2,4-dione. The dianion coordinates with N^1 and N^5 as ligators, see **II**. The dianion forms a bis(didentate) coordination compound with cobalt(III), see **III**.

Scheme 1. [(6*S*,7*S*)-Diphenyl-1,3,5,8,10,12-hexaazadodecane-2,4,9,11-tetraonato(4−)-κ^4 N^1,N^5,N^8,N^{12}]cobaltate(1−), Abbreviated [Co(*S*,*S*-stien(biur)$_2$)]$^-$, **I**

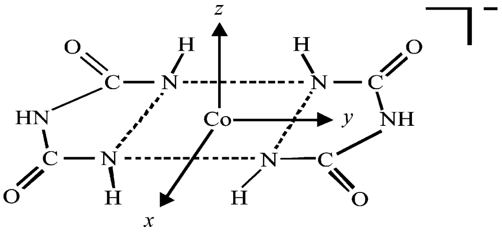


Scheme 2. Biuretate, 1,3,5-Triazapentane-2,4-dionate(2−), Abbreviated biur^{2-}, **II**[a]



[a] The anion is placed in the *yz*-plane of a coordinate system, whose *z*-axis coincides with the 2-fold axis of the point group C_{2v}. The irreducible representation B_1 is defined to have the character equal to +1 under reflection in the *zx*-plane.

Scheme 3. Bis[biuretato(2−)-$6^2N^1,N^5$]cobaltate(1−), Abbreviated [Co(biur)$_2$]$^-$, **III**[a]



[a] The coordinate axes coincide with the three 2-fold axes of the point group D_{2h}.

The compound (6*S*,7*S*)-diphenyl-1,3,5,8,10,12-hexaazadodecane-2,4,9,11-tetraone which was prepared from (1*S*,2*S*)-diphenylethane-1,2-diamine (stilbenediamine, stien) by reaction with nitrobiuret is abbreviated *S*,*S*-stien(biurH$_2$)$_2$.[11] Analogously, the abbreviation *R*-pn(biurH$_2$)$_2$ is used for the compound which was similarly prepared from *R*-propane-1,2-diamine, (±)-bn(biurH$_2$)$_2$ for that prepared from racemic butane-2,3-diamine, and *m*-bn(biurH$_2$)$_2$ for that prepared from *meso*-butane-2,3-diamine.

The coordination compound between cobalt(III) and the anion *S*,*S*-stien(biur)$_2^{4-}$, that is, the complex anion which is abbreviated [Co(*S*,*S*-stien(biur)$_2$)]$^-$ is drawn as **I**. Analogous short names are used for the cobalt(III) compounds derived from the other tetradentate, $\kappa^4N^1,N^5,N^8,N^{12}$ ligands mentioned above.

The cations tetrabutyl ammonium and tetraethyl ammonium are abbreviated Bu_4N^+ and Et_4N^+, respectively.

Preparations. $Et_4N[Co(biur)_2]$. This compound was prepared according to the procedure of Birker et al. for the analogous

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potassium salt using Et_4NOH instead of KOH.[11] Similarly, CsOH was used to prepare cesium salts.[10]

$Bu_4N[Co(\textit{S,S}\text{-stien(biur)}_2)]\cdot H_2O$. $CoCl_2\cdot 6H_2O$ (4.4 g, 18.4 mmol), KOH (8 g, excess), Bu_4NI (6.8 g, 18.4 mmol), and *S*,*S*-stien(biurH_2)$_2$ (7 g, 18.4 mmol) were successively dissolved in 200 mL of water. The mixture was aerated for 16 h while being vigorously stirred. The red precipitate was dissolved in 300 mL of methanol and recrystallized by the addition of 2 L of diethyl ether. Yield: 9.0 g (13 mmol, 73%). Found: C, 58.4; H, 7.78; N, 14.0. Calcd. for $C_{34}H_{54}N_7O_5Co$: C, 58.3; H, 7.97; N, 13.9. The compounds derived from butane-2,3-diamine and propane-1,2-diamine were prepared from $[Co(NH_3)_6]^{3+}$ by a method published earlier.[12]

Instruments. All spectra were measured at room temperature. Absorption spectra were recorded on Cary 118C and 5E spectrophotometers. CD/MCD spectra in UV−vis were obtained using a Jasco 710/720 spectropolarimeter. MCD was measured with a 1.6 T electromagnet and with a 4 T superconducting magnet, SpectroMag III from Oxford Instruments. Each MCD spectrum was obtained as a difference between two recordings, namely, one with the magnetic flux density parallel to the direction of the light beam minus one with the *B*-field antiparallel. NIR-CD was measured on a home-built instrument, and bulk magnetic susceptibilities were obtained by the Faraday method.[13]

Computations. Ligand field computations were performed on ordinary computers using the program Ligfield.[14a] Other programs are on the market, according to the descriptions, can perform such calculations equally well.[14]

Spectral and Magnetic Data. The absorption spectra (ABS) of $[Co(\textit{S,S}\text{-stien(biur)}_2)]^-$ over the range 0.7 μm^{-1} - 4.5 μm^{-1} is shown in Figure 1, together with the associated natural circular dichroism (CD) and magnetic circular dichroism (MCD) of $[Co(\pm)\text{-bn-(biur)}_2)]^-$. Our experimental data are collected in Table 1, together with recent CD-data[15] around 0.4 μm^{-1}.

The magnetic susceptibilities of $Bu_4N[Co(\textit{S,S}\text{-stien(biur)}_2)]\cdot H_2O$ and $Bu_4N[Co(\textit{R}\text{-pn(biur)}_2)]$ were determined at varying magnetic flux densities, $0.26 < B < 1.30$ T, and temperatures, $5 < T < 300$ K. For both compounds, a normal Curie−Weiss behavior was found. The values of μ_{eff} and the Weiss constant, θ, were determined from the linear range (room temperature (RT) $> T >$ 35 K) of the inverse susceptibility χ_m^{-1} versus *T*. For $Bu_4N[Co(\textit{S,S}\text{-stien(biur)}_2)]\cdot H_2O$, μ_{eff} was found to be 3.386, and θ was found to be −11.6 K. For $Bu_4N[Co(\textit{R}\text{-pn(biur)}_2)]$, we found $\mu_{eff} = 3.27$ and θ to be −5.8 K.

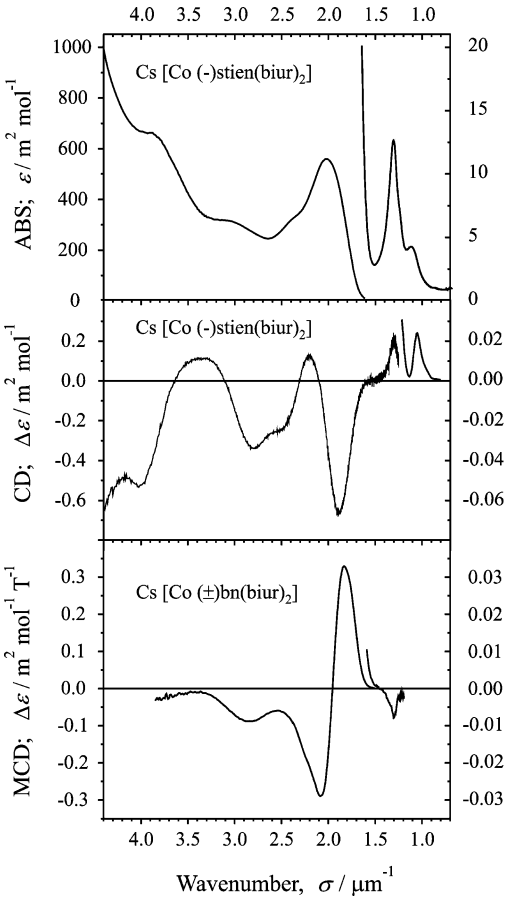

Figure 1. Spectra of $[Co(\textit{S,S}\text{-stien(biur)}_2)]^-$ and $[Co(\pm)\text{-bn(biur)}_2]^-$. Left scales refer to left part of a spectrum, and right scales refer to the right part of a spectrum. Upper panel: Absorption spectrum of $Cs[Co(\textit{S,S}\text{-stien(biur)}_2)]$ in H_2O. Middle panel: Circular dichroism of the same compound in H_2O. Lower panel: Magnetically induced circular dichroism spectrum of $Cs[Co(\pm)\text{-bn(biur)}_2]$ in H_2O; magnetic induction, $B = 4$ T.

Table 1. Experimental Data[a]

wavelength[b]	wavenumber[c]	abs[d]	CD[e]	MCD[f]
	0.3		+0.0002	
	0.4		−0.002	
950	1.05		+0.024	
895	1.12	4		
774	1.29		+0.21	
765	1.31	12		−0.007
556	1.80		−0.5 (sh)	
545	1.83			+0.33
525	1.90		−0.66	
494	2.02	560		
480	2.08			−0.29
454	2.20		+0.13	
417	2.40	320 (sh)		
400	2.50		−0.25	
359	2.79		−0.34	
353	2.83			−0.08
324	3.08	317 (sh)		
300	3.33		+0.11	
258	3.85	663		

[a] Data of the spectra of $Cs[Co(-)\text{stien(biur)}_2]$ in H_2O at room temperature (RT); $Cs[Co(\pm)\text{-bn(biur)}_2]$ in H_2O at $B = 4$T, RT; CD of $Cs[Co(-)\text{stien(biur)}_2]$ in DMSO and NaBr at RT in IR.[15] [b] Wavelength (nm). [c] Wavenumber (μm^{-1}). [d] Absorption coefficient ($m^2\ mol^{-1}$). [e] Circular dichroism ($m^2\ mol^{-1}$). [f] Magnetic circular dichroism ($m^2\ mol^{-1}\ T^{-1}$).

Discussion

The objective of this discussion is to interpret the experimental results using a modern approach to ligand-field methods. It turns out that a combination of DFT calculations, ligand-field calculations in the full Slater−Condon−Racah scheme, and interpretations using a molecular-orbital ap-

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Table 2. Symmetry Labeling of d-Orbitals in Three Point Groups[a]

[b]R_3 $l = 2$	d_{z^2}	d_{yz}	d_{zx}	d_{xy}	$d_{x^2-y^2}$
[c]C_{4v} along z	σ	π sin	π cos	δ sin	δ cos
[d]D_{2h} Scheme 3	a_g	b_{3g}	b_{2g}	b_{1g}	a_g

[a] The three groups are all defined with respect to the same Cartesian coordinate system, as shown in **III**. [b] Marked as the solid spherical harmonics. In the group R_{3i}, they are all even under the inversion, that, gerade, g. [c] Marked after the character under the operation C_∞^z. We shall use the abbreviation πs and πc for the components of the irreducible representation π. [d] Marked after the irreducible representations of the holohedric orthorhombic group.

Table 3. Comparisons between One-Electron Energies Leading to Spin Triplet Ground States[a]

present work[b]		König and Kremer[c]		Komorita et al.[d]	
d_{xy}	2.1	d_{z^2}	1.9	d_{xy}	3.65
d_{yz}	1.1	d_{xy}	1.0	d_{yz}	0.50
d_{zx}	1.0			d_{zx}	0.38
d_{z^2}	0.7	$d_{x^2-y^2}$	0.2	$d_{x^2-y^2}$	0.23
$d_{x^2-y^2}$	0.0	d_{yz}, d_{zx}	0.0	d_{z^2}	0.00

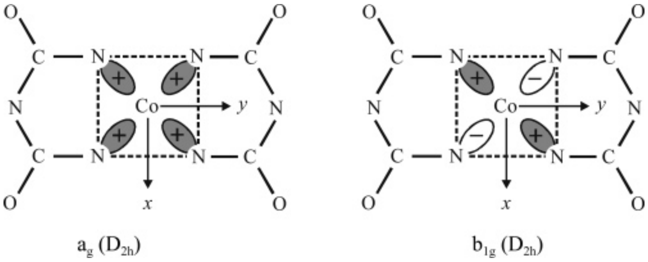
[a] Relative orbital energies of d-orbitals in μm^{-1}; coordinate system is as shown in **III**. [b] Fit of parameters to the spectra of $Bu_4N[Co(-)_D\text{-stien}(biur)_2]$: $e_\sigma = 0.7\ \mu m^{-1}$; $e_\psi = 1.1\ \mu m^{-1}$; $e_\chi = 1.0\ \mu m^{-1}$. See Figure 5. [c] Ligand-field calculation: $Dq = 0.08\ \mu m^{-1}$; $Ds = 0.10\ \mu m^{-1}$; $Dt = 0.10\ \mu m^{-1}$.[8b] [d] Extended Hückel MO calculation.[26]

proach greatly improve the chemists understanding of chemical bonding in coordination compounds.[16]

As pointed out in the introduction the parameters *Dq*, *Ds*, and *Dt* of crystal-field theory are not useful, despite the fact that the calculations were carried out using the Slater−Condon−Racah scheme with the two-electron parameters B_{Racah} and C_{Racah}.[8] The angular overlap model, AOM,[17] can successfully treat σ-bonding and simple π-bonding, but it does not work for four-coordinate planar complexes with multidentate π-conjugate ligands.

The theory of this type of ligand was first attacked by Orgel in 1961.[18] He studied tris-complexes of symmetric ligands with conjugated π-systems such as 1,10-phenantroline. In such ligands the π-MO's may be classified according to their symmetry with respect to reflection in the symmetry plane perpendicular to the plane of the molecule. Those which remain unchanged under this symmetry operation are given the label ψ (Figure 3). The reason for the symbol ψ is that the frontier orbitals have the positive lobes pointing in the same direction and thereby look like that letter. For similar reasons, the label χ marks the π-MO's which change sign under the reflection (Figure 4). We follow this custom in the present paper.

Ceulemans et al. (1985) called this kind of coordinating ligand for "phase-coupled" ligands, thereby indicating the MO character of the interaction. However, in a subsequent work on planar coordination compounds, the authors emphasize that the two didentate π-conjugated ligands are electronically isolated.[5]



a_g (D_{2h}) b_{1g} (D_{2h})

Figure 2. Ligand σ-orbitals. Only the lone pairs of nitrogen are drawn. The ligators are numbered, starting from the upper left and running with the clock. The two gerade functions are $(+\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)/2$ which transforms as a_g and $(+\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)/2$ which transforms as b_{1g}

Schäffer and Yamatera (1991) made a thorough study of the binding modes of "Orgel-ligands".[6] In the case of bis-didentate compounds, they moved the focus from the ligands to the d-orbitals. In fact, they used *ligand-adapted d-orbitals* and did not arrive at usefull expressions for the ligand field matrix (see eq 7 below).

Gerloch et al. (1997) reviewed this discussion, in particular Schäffer and Yamatera's contribution. However, they continued the use of ligand-adapted 3d-orbitals and did not reach a workable solution in their article.[19]

To overcome these difficulties, we now introduce the *molecules-in-molecules* concept. By this we mean that *the total ligand system is treated as one entity*. In the language of ligand-field theory, we consider the perturbation of the complete ligand onto the unperturbed d-orbitals. This perturbation is divided into two parts. One is that of σ-bonding which is treated equivalently to the AOM. The other one is that of the π-bonding which is treated differently such that it takes into account the symmetry of the whole π-system.

Model. Any ligand-field scheme requires a model for the one-electron matrix (eq 2), which represents the effect of the ligand on the partially filled d-shell of the metal. A main point in this discussion is that the word ligand is singular, meaning that all ligating entities are treated as one ligator. The orbitals which give rise to the one-electron matrix are supposed to be linear combinations of metal d-orbitals and ligand σ- and π-orbitals.

Although no experimentally determined structure is available for $[Co(biur)_2]^-$, we shall use the point group D_{2h} to characterize the various orbitals. Thus, we assume the structure shown as **III,** and the aim is to create the five by five matrix

$$\{3d|V(\text{all } p; \boldsymbol{r}_i)|3d\} \tag{2}$$

where $|3d\}$ is the row vector ($3d_{z^2}$, $3d_{yz}$, $3d_{zx}$, $3d_{xy}$, $3d_{x^2-y^2}$) and $\{3d|$ is the transposed vector (a column vector). The ligand field operator V is an one-electron operator which is a function of the type and position of all p ligands and of the electron coordinate $\boldsymbol{r}_i$.[20]

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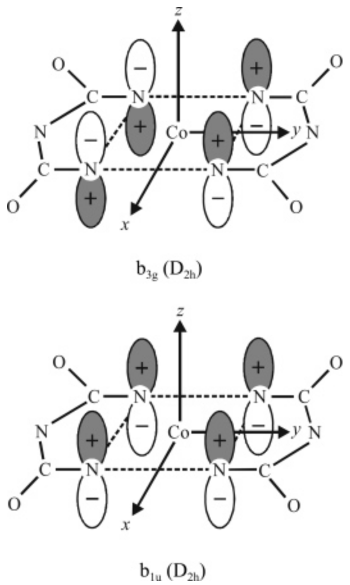
(20) Details of the construction of the matrix, eq 2, are given in Supporting Information, sections S4 and S5.



b_{3g} (D_{2h})

b_{1u} (D_{2h})

Figure 3. Ligand ψ-orbitals in the 1π, 3π, 5π, and 7π MO's of biuretate. Only the nitrogen p-AO's are drawn. The right-hand ligand is called *a*, and the other one is *b*. The ψ-functions are $(+\psi_a + \psi_b)/\sqrt{2}$ which transforms as b_{3g} and $(+\psi_a - \psi_b)/\sqrt{2}$ which transforms as b_{1u}

***σ*-Bonding.** The ligand σ-MO's are shown in Figure 2. They transform as a_g, b_{1g}, b_{2u}, and b_{3u} in the point group D_{2h}. The gerade orbital a_g may interact with the two metal σ orbitals 4s and $3d_{z^2}$ which both transform as a_g. The other gerade orbital b_{1g} may interact with the metal σ orbital $3d_{xy}$ which transforms as b_{1g}, see Table 2. The ungerade ones cannot interact with d-orbitals.

It follows directly from the symmetry properties of d-orbitals that if we in the matrix, eq 2, put

$$\langle 3d_{z^2}\,(a_g)|\,V(\text{all } p;\, \boldsymbol{r}_i)|\,3d_{z^2}\,(a_g)\rangle = e_\sigma \tag{3}$$

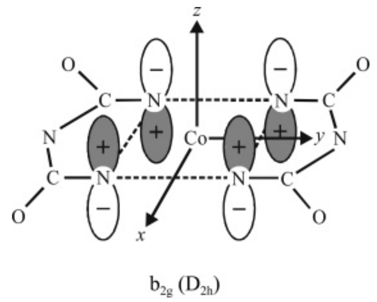
then

$$\langle 3d_{xy}\,(b_{1g})|\,V(\text{all } p;\, \boldsymbol{r}_i)|\,3d_{xy}\,(b_{1g})\rangle = 3\,e_\sigma \tag{4}$$

and all other elements are zero. We take this as the e_σ part of the matrix, eq 2, but note that the ratio 1:3 is not required in the group D_{2h}. In fact, the D_{2h} point group allows mixing between the two σ3d-orbitals, transforming as a_g, and the metal 4s-orbitals; this must introduce an uncertainty for the energy of the σ3d-orbitals when estimated by a ligand field method.

***π*-Bonding.** The biuretate dianion, **II**, contains a conjugate π system built up of the seven p-orbitals which are perpendicular to the *yz*-plane. According to simple Hückel theory, they may form seven πMOs, of which five are occupied.[21] The most stable of these, 1π, transforms as b_1 in the point group C_{2v} and so do all the odd-numbered πMOs, whereas all the even-numbered πMOs transform as a_2 in this point group. Thus, the $5\pi\psi$ is a HOMO, and the $6\pi\chi$ is a LUMO.

The frontier orbitals of the ligand πMOs of the tetradentate ligand **III** are shown in Figures 3 and 4. They transform as ψb_{3g}, ψb_{1u}, χb_{2g}, and χa_u in the point group D_{2h}. The ψb_{3g} orbital may interact with the $d_{\pi s} = d_{yz}$ orbital of the metal to give the collective parameter



b_{2g} (D_{2h})

Figure 4. Ligand χ-orbitals in the 2π, 4π, and 6π MO's of biuretate. Only the nitrogen p-AO's are drawn. The right-hand ligand is called *a*, and the other one is *b*. The gerade χ-function is $(+\pi_a + \pi_b)/\sqrt{2}$ which transforms as b_{2g}

$$\langle 3d_{yz}\,(b_{3g})|\,V(\text{all } p;\, \boldsymbol{r}_i)|\,3d_{yz}\,(b_{3g})\rangle = e_\psi \tag{5}$$

and analogously, the χb_{2g} orbital may interact with the $d_{\pi c} = d_{zx}$ orbital of the metal to give the collective parameter

$$\langle 3d_{zx}\,(b_{2g})|\,V(\text{all } p;\, \boldsymbol{r}_i)|\,3d_{zx}\,(b_{2g})\rangle = e_\chi \tag{6}$$

These two parameters describe the only nonvanishing elements of the matrix, eq 2, resulting from π-bonding.

Finally, it is noted that the $d_{x^2-y^2}$ orbital with a_g symmetry is a nonbonding orbital. The overall result is that the one-electron matrix, eq 2, reduces to the diagonal matrix

$$\{3d|\,V(\text{all } p;\, \boldsymbol{r}_i)|\,3d\} = \text{diag}(e_\sigma, e_\psi, e_\chi, 3e_\sigma, 0) \tag{7}$$

Calculations. Complete algorithms for ligand-field calculations in the Slater−Condon−Racah scheme have been published, and programs for personal computers have been available in public since 1990.[22] Recent programs have the advantage that the above π-parametrization can be included.[14] We have used the Ligfield program,[14a] which has the possibility of a direct input of the one-electron matrix,[23] eq 7, and of calculating energy level diagrams of a d^6-electron configuration with the Racah parameters, B_{Racah} and C_{Racah}. Computations with this program gave the parameters

$$e_\sigma = 0.7\,\mu\text{m}^{-1},\ e_\psi = 1.1\,\mu\text{m}^{-1},\ e_\chi = 1.0\,\mu\text{m}^{-1} \tag{8a}$$

$$B_{\text{Racah}} = 0.05\,\mu\text{m}^{-1},\ C_{\text{Racah}} = 4B_{\text{Racah}} \tag{8b}$$

as a good guess. It fits the available experimental data for four-coordinate planar species $[\text{Co(biur)}_2]^-$ with point group symmetry D_{2h}. The caption of Table 4 shows the assignments, and below we have we have discussed how this result was achieved.

The one-electron parameters, eq 8a, give rise to the molecular orbital diagram shown in Figure 5. The e_ψ and e_χ parameters embrace all the four ligating N^- entities, corresponding to the single nitrogen π-parameters of 0.275 and

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(21) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

(22) (a) Harnung, S. E.; Schäffer, C. E. *Struct. Bonding* (*Berlin*) **1972**, *12*, 257−295. (b) Harnung, S. E.; Mønsted, O. Ligand Field Calculations on a Personal Computer, A package of software programs presented at the 28th ICCC, Gera, 1990.

(23) In the Ligfield package these files have the extension .oem.

Table 4. Calculated Energies and Occupation Numbers of Low Lying Electronic States[a]

state	E (μm^{-1})	$d_{x^2-y^2}$	d_{z^2}	d_{zx}	d_{yz}	d_{xy}	occ. no.	pol
$^3B_2$	2.28	1.05	1.01	1.93	0.95	1.06	2.0	
^3A	2.27	1.02	1.97	1.00	1.00	1.01	1.0	
^3A	2.20	1.03	1.93	1.01	0.99	1.04	1.0	
^3A	1.98	1.03	1.97	1.00	1.00	1.00	1.0	z
^3A	1.96	1.38	1.00	1.57	1.55	0.49	1.6	
$^3B_3$	1.95	1.74	0.35	1.03	1.91	0.97	1.9	
$^3B_2$	1.88	1.62	0.62	1.77	1.12	0.88	1.7	
$^3B_1$	1.75	1.60	1.36	0.65	1.38	1.01	1.4	
$^3B_2$	1.72	1.21	1.49	1.29	1.64	0.38	1.3	
$^3B_3$	1.67	1.10	1.77	1.79	1.11	0.24	1.1	
^3A	1.43	1.95	1.05	1.00	1.00	1.00	1.0	z
^3A	1.43	1.73	1.02	1.24	1.24	0.76	1.2	
$^3B_1$	1.33	1.92	1.08	1.42	0.59	1.00	1.4	
^3A	1.21	1.84	1.01	1.15	1.15	0.85	1.1	
$^3B_2$	1.04	1.94	1.92	0.14	1.03	0.97	1.0	x
$^3B_3$	0.95	1.94	1.94	1.03	0.11	0.97	1.0	y
$^3B_2$	0.40	1.97	1.02	1.01	1.97	0.04	1.0	x
$^3B_3$	0.30	1.97	1.02	1.97	1.01	0.03	1.0	y
$^3B_1$	0.00	1.99	1.97	1.00	1.00	0.03	0.0	

[a] Energies of the lowest-spin triplet states of the $3d^6$ configuration of $[Co(biur)_2]^-$ as calculated with the parameters of eq 8. These states together with a quintet state and a few singlet states are depicted in the center of Figure 6 at ($w = 1$, $x = 1$). From left, the columns show the symmetry in point group D_2, the energy of the state, the occupation number of the five d-orbitals (each accounts for two spin-orbitals), the change of occupation number when a state is excited from the ground state, and the polarization of the electric transition moment with coordinate system as shown in **III**.

assignments of d-d transitions

$^3A \leftarrow {}^3B_1$	1.9 μm^{-1}(obsd)	1.98 μm^{-1} (calcd)	appr	$d_{xy} \leftarrow d_{x^2-y^2}$
$^3A \leftarrow {}^3B_1$		1.43 μm^{-1} (calcd)	appr	$d_{xy} \leftarrow d_{z^2}$
$^3B_2 \leftarrow {}^3B_1$	1.3 μm^{-1} (obsd)	1.04 μm^{-1} (calcd)	appr	$d_{xy} \leftarrow d_{zx}$
$^3B_3 \leftarrow {}^3B_1$	1.1 μm^{-1} (obsd)	0.95 μm^{-1}(calcd)	appr	$d_{xy} \leftarrow d_{yx}$
$^3B_2 \leftarrow {}^3B_1$	0.40 μm^{-1} (obsd)	0.40 μm^{-1} (calcd)	appr	$d_{yz} \leftarrow d_{z^2}$
$^3B_3 \leftarrow {}^3B_1$	0.3 μm^{-1} (obsd)	0.30 μm^{-1}(calcd)	appr.	$d_{zx} \leftarrow d_{z^2}$

assignments of MCD transitions (for data, see Table 1)

1.83 μm^{-1} (obsd) $\Delta\epsilon = +0.33$ m^2 mol^{-1} T^{-1}	$d_{zx} \leftarrow 5\pi b_{1u}$
2.08 μm^{-1} (obsd) $\Delta\epsilon = -0.29$ m^2 mol^{-1} T^{-1}	$d_{yz} \leftarrow 5\pi b_{1u}$
2.83 μm^{-1} (obsd) $\Delta\epsilon = -0.08$ m^2 mol^{-1} T^{-1}	$d_{xy} \leftarrow 5\pi b_{1u}$

0.25 μm^{-1}, respectively. This gives the ratio between σ and π parameters, $r(N^-) = e_\sigma/e_\pi \approx 3$, which may be compared with the following ratios which were found for a series of chromium(III) coordination compounds: $r(H_2O) \approx 4$; $r(OH^-) \approx 4$; $r(F^-) \approx 4$; $r(Cl^-) \approx 7$; and $r(Br^-) \approx 10$.[25] The ratio found here demonstrates that the ligand N^- in $[Co(biur)_2]^-$ is strongly π-interacting with the 3d-orbitals. This may well be the reason for the unusual geometry and spin state for these cobalt(III) coordination compounds.

Figure 6 shows an extended Tanabe−Sugano energy-level diagram based on the parameters of eq 8. To create this, the two dimensionless parameters w and x are introduced

$$e_\sigma = 0.7w\ \mu\text{m}^{-1},\ e_\psi = 1.1w\ \mu\text{m}^{-1},\ e_\chi = 1.0w\ \mu\text{m}^{-1} \qquad 0 \le w \le 1 \quad (9a)$$

$$B_{\text{Racah}} = 0.05\,x\ \mu\text{m}^{-1},\ C_{\text{Racah}} = 0.20\,x\ \mu\text{m}^{-1} \qquad 1 \ge x \ge 0 \quad (9b)$$

All allowed values of w and x describe a planar coordination compound $[Co(biur)_2]^-$. The “weak-field scheme” is given by $0 \le w \le 1$ and $x = 1$; for $w = 0$, one has an accidental degeneracy corresponding to spherical symmetry, and the ground state is a spin quintet. The “strong-field scheme” is given by $w = 1$ and $1 \ge x \ge 0$; for $x = 0$, one has no electronic repulsion, and the ground state is a spin singlet. For $w = x = 1$, eq 8 is retrieved.

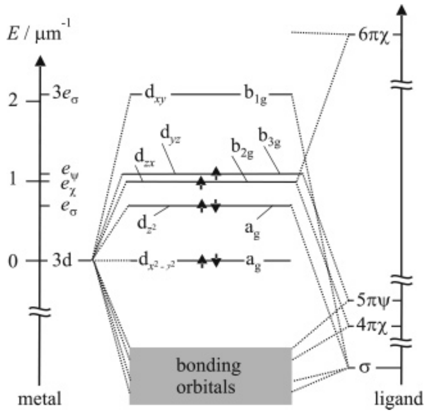

Figure 5. Molecular orbital diagram for $[Co(biuret)_2]^!$ described in the point group D_{2h}. The diagram represents the ligand field splitting of the metal 3d-orbitals. The relative energies of these orbitals can be drawn to scale because the perturbation matrix, eq 7, is diagonal (see Table 3). The orbital $d_{x^2-y^2}$ (a_g) is a nonbonding orbital. The orbitals d_{z^2} (a_g) and d_{xy} (b_{1g}) are σ-antibonding. The orbital d_{yz} (b_{3g}) is π-antibonding; its energy is the result of the odd-numbered ligand molecular orbitals, all of symmetry ψ. The orbital d_{zx} (b_{2g}) is π-antibonding; its energy is the result of the even-numbered ligand molecular orbitals, all of symmetry χ. In the ligand, the energy difference between the HOMO ($5\pi\psi$) and the LUMO ($6\pi\chi$) is >5.2 μm^{-1}; accordingly, the latter has very little effect on the d_{zx} orbital. The arrows represent the distribution of electrons in the ground state, see Table 4.

We have used the *Ligfield* program to test two interesting cases.

(1) If the energy difference between the ligand HOMO and LUMO is small, then the $d_{zx}(\chi)$ orbital may be a bonding orbital. The choice $e_\sigma = 1.0\,y\ \mu$m^{-1}, $e_\psi = 0.5\,y\ \mu$m^{-1}, $e_\chi = -0.2\,y\ \mu$m^{-1}, $B_{\text{Racah}} = 0.08\ \mu$m^{-1}, and $C_{\text{Racah}} = 3B_{\text{Racah}}$ for varying values of the number y, $0 \le y$, mimics this case. The ensuing ground states as function of the parameter y are

$$^5B_2\ (0 < y < 0.65);\ {}^3B_3\ (0.65 < y < 1.5);\ {}^1A(1.5 < y)$$

showing that in the *molecules-in-molecules* model the spin triplet obtains a rather wide range of ligand-field parameters.

(2) The parameters of eq 8 but with $e_\psi = e_\chi = 1.05\ \mu$m^{-1} yield a D_{4h} approximation to our actual D_{2h} symmetry parameters. This set of parameters describes the case where the distance between the ligand HOMO and LUMO is large. One finds the lowest ^3E (corresponding to the lowest pair of $^3B_3$ and $^3B_2$, see Table 4 and Figure 6) at 0.35 μm^{-1} above the $^3A_2$ ground state. The next ^3E is found at 0.99 μm^{-1}. These two D_{4h} transitions correspond to the infrared and near-infrared transitions described in this paper.

Determination of Parameters. It is not yet feasible to transform all experimental data into the parameters in a strict mathematical/statistical way, and therefore, the present analysis has been guided by comparisons with the literature and trial-and-error fitting to the observations. The analysis

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(24) Larsen, E.; Thulstrup, P. W. *Dalton Trans.* **2006**, 1784−1789.

(25) (a) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399−1407. (b) Schäffer, C. E. *Pure Appl. Chem.* **1970**, *24*, 361−392.

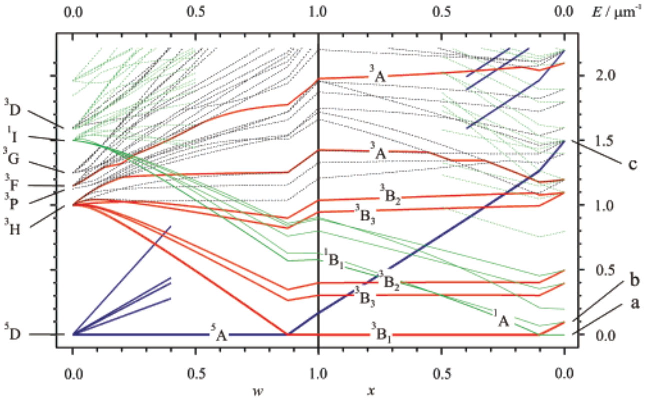

Figure 6. Modified Tanabe−Sugano energy level diagram. Left panel: Energy levels for weak to moderate ligand field, $0 \leq w \leq 1$, $x = 1$. Right panel: Energy levels for moderate to strong ligand field, $w = 1$, $1 \geq x \geq 0$. The dependence of the energy levels as functions of w is defined in eq 9a and their dependence of x in eq 9b. The parameters describe a four-coordinate planar species $[Co(biur)_2]^-$; only the lowest excited states, $E < 2.1$ μm^{-1}, are shown. The energies for ($w = 1$, $x = 1$) are given in Table 4. Singlets are marked with green, quintets with blue, and triplets are shown as red lines or black dashes. The red lines indicate levels to which transitions are expected to be more intense. The heavy lines indicate ground states for some choices of the parameters w and x. The observed triplet transitions and the lowest spin singlet, $^1B_1$, are labeled. For ($w = 0$, $x = 1$), one has a spherical symmetric d^6 electronic system whose term symbols are shown to the left. For (small w, $x = 1$), one has the weak-field scheme, that is, the symmetry of the complex is correct, but the ligand field is small. Here the ground state is a spin quintet, ^5A. For ($w > 0.88$, $x = 1$), the spin triplet, $^3B_1$, becomes the ground state. For ($w = 1$, $x = 0$), one has the strong-field scheme, where the wave functions are single, normalized Slater determinants. A few are marked: (a) $|(d_{x^2-y^2})^2\,(d_{z^2})^2\,(d_{zx})^2\,(d_{yz})^0\,(d_{xy})^0\,|/\sqrt{6}$ giving rise to 1 ^1A, (b) $|(d_{x^2-y^2})^2\,(d_{z^2})^2\,(d_{zx})^1\,(d_{yz})^1\,(d_{xy})^0\,|/\sqrt{6}$ giving rise to 1 $^3B_1$ and 1 $^1B_1$, and (c) $|(d_{x^2-y^2})^2\,(d_{z^2})^1\,(d_{zx})^1\,(d_{yz})^1\,(d_{xy})^1\,|/\sqrt{6}$ giving rise to 1 ^5A, 3 ^3A, and 2 ^1A. Only for ($w = 1$, $x < 0.1$), one has a spin singlet ground state, ^1A.

includes experimental results of several, similar componds, and this alone shows the qualitative nature of the fit. During the work, we have also been guided by DFT calculations.[24] It has been pointed out[16] that ligand-field theory and DFT calculations stimulate one another, and we consider that one way to pursue this point is to make analyses as done here.

Parameter values in the range of $e_\sigma = 0.6-0.8$ μm^{-1}, $B_{\mathrm{Racah}} = 0.05-0.07$ μm^{-1}, and $C_{\mathrm{Racah}}/B_{\mathrm{Racah}} = 3-4$ are generally accepted,[25] and we have imposed these limits on the three parameters. Accordingly, the following discussion is concerned only with the limits of the two e_π parameters, e_ψ and e_χ.

All odd numbered π-orbitals in biur^{2-} contribute to the ligand ψ character, and all even-numbered π orbitals contribute to the ligand χ character. Because the biur^{2-} HOMO (5π) is of ψ character and at a lower energy than that of the 3d orbitals, one expects $d_{yz}(\psi)$ to be antibonding, that is, $e_\psi > 0$. Similarly, because the biur^{2-} LUMO (6π) is of χ character and of higher energy than that of the 3d orbitals, one might expect $d_{zx}(\chi)$ to be bonding, that is, $e_\chi < 0$. However, experiments indicate that the latter statement is not correct. The free-biuret molecule has a strong absorption ($6\pi \leftarrow 5\pi$) above 5 μm^{-1}. This large energy separation between the 5π and 6π orbitals indicates very little interaction between the 6π and the 3d orbitals. We therefore take the $d_{zx}(\chi)$ orbital to be antibonding as well, and the relation $e_\pi > e_\chi > 0$ is suggested by the MCD. Note in particular that the observed difference in energy between $^3B_3$ and $^3B_2$ is around 0.1 μm^{-1} (vide infra), reflecting the difference, 0.10 μm^{-1}, between d_{yz} and d_{zx}. This observation excludes a description using the point group D_{4h}.

A good set of parameters is given in eq 8. Again we shall stress that e_σ is not well determined from our observed transitions. We believe from dissolving the positive CD components in gaussians that a d−d transition near 1.9 μm^{-1} is seen under the charge-transfer band, and it is interpreted as $d_{xy} \leftarrow d_{x^2-y^2}$ for which a CD is expected because of the large magnetic transition moment, $e_\sigma = 1.9/3 \approx 0.6$ μm^{-1} based on this assignment. From the infrared and near-infrared transitions, we estimate e_σ to be 0.7 μm^{-1}. The uncertainty about the value of e_σ and in particular the position of the $d_{x^2-y^2}$-orbital may be attributable to an interaction between the 4s- and the set of totally symmetric 3d-orbitals: $3d_{x^2-y^2}$ and $3d_{z^2}$. However, we have no experimental data that indicate such an interaction, and we do not need it for the description.

Electronic Ground State. The magnetic susceptibility data show clearly that the electronic ground state is a spin-triplet state. A general result of using the molecules-in-molecules concept is the wide range of parameters allowing a ground state triplet from the calculations. It is obtained by use of quite realistic energy parameters as discussed in connection with Figure 5 above.

Table 3 shows a comparison of d-orbital splittings which in each particular scheme of calculation give rise to a spin-triplet ground state. It appears that neither the crystal-field nor the extended Hückel MO method give a chemically satisfactory ordering of the d-orbitals.

It is noted that there is no need to include spin−orbit coupling in our interpretations, but reservations to which degree the 4s-orbital contributes to the energy of the a_g orbitals must be made.

Intensities of d−d Transitions. A necessary condition for an electronic transition to take place (i.e., being observable) between states, whose wave functions are single Slater determinants, is that the occupation number between the two states differs by just one.[27]

Figure 6 shows part of the ligand field calculations. When one “moves” in the “strong-field scheme”, that is, when the parameter x grows from 0 toward 1, the states become linear combinations of Slater determinants. In this way, originally forbidden two-electron transitions may borrow intensity and allowed one-electron transitions may lose intensity. The most intense of (the parity-forbidden) d−d transitions are expected to be those which have the change of occupation number near one. Our results are shown in Table 4. Note the dramatic reduction of the number of expected observable d−d transitions relative to the number, calculated in the ligand-

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(26) Komorita, T.; Fujita, M. B.; Kanamori, K.; Hayashi, S.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2163−2172. The data are extracted from Figure 1.

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field scheme. (In the d^6 electron configuration, a total of 210 functions gives $(135/3 - 1) = 44$ triplet−triplet transitions in the point group D_2 without spin−orbit coupling.) Note also that the one-electron transitions which emerge from this analysis are exactly those that follow from a direct use of Figure 5 (see also the caption to Table 4).

Assignments. All M[Co(biur)$_2$] with M^+ equal to K^+, Cs^+, Et_4N^+, and Bu_4N^+ possess very limited solubility in translucent solvents. Therefore, we have measured the spectral properties of derivatives such as $[Co(R\text{-pn(biur)}_2)]^-$, $[Co((\pm)\text{-bn(biur)}_2)]^-$, and $[Co(S,S\text{-stien(biur)}_2)]^-$. The lowering of the symmetry group from D_{2h} to D_2 is supposed to be of minor significance for energy levels but much more important for intensities and of course decisive for CD. The different complexes show spectra which are very similar, but they are of course not identical. The variation between spectral maxima shows that our ligand-field treatment has a natural limiting accuracy for the data from the whole group of coordination compounds.

The assignments of the d−d transitions have been guided by the change in occupation numbers being close to one for the most intense transitions, see Table 4. It turns out that only a few transitions among the many calculated ones are expected to have an observable intensity. Using the fact that the ground state is a spin-triplet, that the transitions at 0.3, 0.4, 1.1, and 1.3 μm^{-1} are d−d transitions, and that part of the transition at 1.9 μm^{-1} is d−d as well, we have arrived at the assignment shown in Figure 6 at $w = 1$, $x = 1$.

The natural circular dichroism of **I** is shown in Figure 1. In the 1.0−1.3 μm^{-1} region, the spectrum exhibits two positive CD components separated by a shallow trough indicating the presence of a negative CD component. We consider that this CD confirms the assignments for three out of the four one-electron transitions. Recently,[15] the CD in the infrared region has become available, and the lowest two d−d transitions are clearly discernible, see Table 1. A weak MCD at 1.3 μm^{-1} has been observed.

The charge transfer (CT) spectra are ligand-to-metal transitions. The MCD spectrum shows clearly three *B*-term components (peaks at 1.83, 2.08, and 2.83 μm^{-1}) which are assigned as excitations from an ungerade ligand π orbital, $5\pi b_{1u}$, to $3d_{zx}$, $3d_{yz}$, and $3d_{xy}$, respectively. The absorptions up to 5 μm^{-1} are likewise considered to be charge transfers from, for example, $4\pi a_u$, $3\pi b_{1u}$, and ungerade ligand σ orbitals to the 3d orbitals. The closeness (0.1 μm^{-1}) of the two transitions from $5\pi b_{1u}$ to $3d_{zx}$, $3d_{yz}$ might look surprising, but we were forced from this fact to consider e_χ positive, that is, associated with an antibonding character of the $3d_{zx}$ orbital, because the 4π interactions dominates over the 6π interactions. Accordingly, $e_\psi - e_\chi \approx 0.1\ \mu m^{-1}$. The difference between the mean of the first two MCD components and the third one is close to 0.8 μm^{-1}. This is the difference we expect between the two $3d_{xz}$, $3d_{yz}$ orbitals and the $3d_{xy}$ orbital, and this defines the parameter e_σ (see Figure 5).

The CT absorption band near 2 μm^{-1} has two CD components which may be assigned to the same transitions as those which gave rise to the MCD-spectrum.

Final Remarks. A recent DFT study of bis(biuretato)-cobaltate(1−) coordination compounds draws conclusions on the mixing of cobalt(III) 3d-orbitals and $(biur)_2^{4-}$ π-orbitals which are consistent with the ideas developed here.[24]

From the Kohn−Sham orbitals obtained from that study it is very clear that $2\pi b_{2g}$ and $4\pi b_{2g}$ both have strong overlaps with the d_{zx}-orbital, whereas the empty $6\pi b_{2g}$-orbital has a significantly smaller overlap; this leads to the positive value for e_χ. The low-lying πb_{2g}-orbitals simply dominate the overlap. The $5\pi b_{3g}$ has a strong overlap to d_{yz} just as also $1\pi b_{3g}$. Both $3\pi b_{3g}$ and $7\pi b_{3g}$ have negligible overlaps with d_{yz} leading to the positive e_ψ. The 4s-orbital on cobalt(III) participates in the a_g orbitals dominated by d_{z^2} and $d_{x^2-y^2}$. It is generally accepted that DFT calculations produce results that overestimate the covalency. This, we believe, is also the case for those computations which mix up to 20% of 4s-orbital into the d-orbitals. However, consistent interpretation of our experimental data need not invoke explicitly the s-influence on the energy parameters.

The molecules in molecules approach is easy to extend to a ligand-field treatment of tris(didentate) coordination compounds of planar, π-conjugated ligands.[28]

Acknowledgment. Support from Danish Natural Science Research Council (21-04-0089) is gratefully acknowledged, and E.L. also gratefully acknowledges COST D21 chemistry collaboration for helpful discussions (D21-007). We thank Professor J. Bendix for a copy of the program Ligfield.[14]

Supporting Information Available: Material of mathematical nature. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Harnung, S. E.; Larsen, E. Unpublished work.