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Preparation, Structure, and Spectroscopy of Cobalt(III) Complexes Containing *N,N'*-Di-8-quinolyl Derivatives of 1,2-Diaminoethane, (*R*)-1,2-Diaminopropane, and (*R,R*)-1,2-Diaminocyclohexane

TOSHISHIGE M. SUZUKI,¹ SIGERU OHBA,² SHOICHI SATO,³ YOSHIHIKO SAITO,² and KAZUO SAITO*

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Mixed-ligand cobalt(III) complexes have been prepared by the reaction of tris(acetylacetonato)cobalt(III) with an *N,N'*-di-8-quinolyl-1,2-diaminoalkane (1,2-diaminoethane, (*R*)-1,2-diaminopropane, and (*R,R*)-1,2-diaminocyclohexane) in organic solvents. The isolated complexes have deprotonated secondary amino nitrogens. The parent complexes with neutral ligands were readily formed on addition of hydrogen chloride in organic solvents, but the crystals were isolated with difficulty. The absorption, CD, and ¹H NMR spectra change rapidly and reversibly on protonation and deprotonation of the quadridentate ligand. The X-ray crystal structure analysis of [Co(acac)(*R*-dqpn')]ClO₄, which contains the deprotonated form of dqpn (dqpn = *N,N'*-di-8-quinolyl-1,2-diaminopropane), has been performed in order to clarify the detailed structure. Crystal data: CoClO₄N₄C₂₆H₂₆, *a* = 11.112 (2) Å, *b* = 13.299 (5) Å, *c* = 9.275 (4) Å, α = 106.06 (4)°, β = 88.72 (3)°, γ = 85.87 (3)°, space group *P*1, *Z* = 2, *R* = 5.7% for 4327 observed reflections. The two independent complex cations consist of the Δ- and Λ-isomers. The stereochemistry including geometrical and optical isomerism of both the protonated and deprotonated complexes is discussed on the basis of the crystal structure and spectroscopic data in solution. The quadridentate ligands seem to undergo rapid rearrangement on protonation and deprotonation of the complexes.

Much attention has been drawn to the cobalt(III) complexes with multidentate ligands structurally intermediate between aliphatic and aromatic systems.⁴⁻¹⁷ Most of the ligands so far used in the preparation of cobalt(III) complexes, however, have been limited to pyridine derivatives. 2-Pyridylmethylamine,^{4,7} 1-(2-pyridyl)ethylamine,⁹⁻¹² and their quadridentate derivatives^{5,6,8,13-15} have partial aromatic character, but the spectroscopic and stereochemical properties of their cobalt(III) complexes are essentially the same as those with aliphatic diamines.

Reaction of various aliphatic diamines with 8-quinolinol gives linear quadridentate ligands in which two amino groups are linked by 8-quinolyl rings.¹⁶ Nielsen and Dahl prepared *N,N'*-di-8-quinolyl derivatives of ethylenediamine and trimethylenediamine and studied the IR and visible absorption spectra of their copper(II) and nickel(II) complexes.¹⁷ One of the present authors studied the CD spectra of copper(II) complexes of related optically active ligands shown in Figure 1.¹⁸ In the present study we have prepared cobalt(III) complexes with these ligands. Reaction of tris(acetylacetonato)-cobalt(III) with the ligand in organic solvent gave a dark purple compound containing the quadridentate ligand in the deprotonated form, [Co(acac)(deprotonated dqdm)]⁺ (acac = acetylacetonato ion; dqdm = *N,N'*-di-8-quinolyl-1,2-diaminoalkane; hereinafter deprotonated dqdm is expressed by

ddqm'). Their preparation, structure, and properties are given in this paper.

Experimental Section

Ligands. *N,N'*-Di-8-quinolyethylenediamine was prepared according to the method described by Jensen and Nielsen.¹⁶ The optically active analogues were prepared as stated previously.¹⁸ The structures and the abbreviations of ligands are shown in Figure 1.

[Co(acac)(dqpn')]ClO₄. A benzene solution of dqpn (0.62 g in 10 cm³) was refluxed with a mixture of [Co(acac)₃] (0.71 g) and LiClO₄·3H₂O (0.64 g) in ethanol (20 cm³) for 1 h. The deep green color changed to intense purple during the course of the reaction. The solution was set aside at room temperature overnight to give black crystals, which were filtered off, washed with ethanol and diethyl ether, and air-dried; yield 0.92 g.

[Co(acac)(*R*-dqpn')]ClO₄. This compound was prepared similarly by use of *R*-dqpn in place of dqpn; yield 0.71 g.

[Co(acac)(*R,R*-dqchxn')]ClO₄. A benzene solution of *R,R*-dqchxn (0.73 g in 10 cm³) was refluxed for 2 h with a mixture of [Co(acac)₃] (0.71 g) and LiClO₄·3H₂O (0.64 g) in ethanol (20 cm³), evaporated to half-volume, and set aside at room temperature overnight. The dark purple crystals were filtered off, washed with diethyl ether, air-dried, and recrystallized from ethanol; yield 0.53 g.

The analytical data of the complexes are summarized in Table I. The three complexes are soluble in polar organic solvents such as methanol, acetone, and dimethyl sulfoxide, are slightly soluble in benzene, and are insoluble in diethyl ether and hexane. They decompose on addition of water to give dark brown solutions.

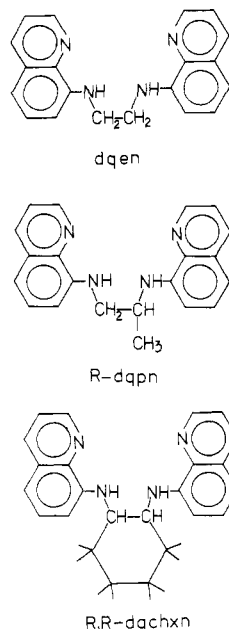
Structure of the Deprotonated [Co(acac)(*R*-dqpn')]ClO₄ Studied by X-ray Crystallography. The crystal data are as follows: [Co(C₂₁H₁₉N₄)(C₅H₇O₂)]ClO₄, [C₂₆H₂₆CoN₄O₂]⁺[ClO₄]⁻, fw 584.4, triclinic, space group *P*1, *a* = 11.112 (2) Å, *b* = 13.299 (5) Å, *c* = 9.275 (4) Å, α = 106.06 (4)°, β = 88.72 (3)°, γ = 85.87 (3)°, *V* = 1312.5 (7) Å³, *Z* = 2, *D*_{meas} = 1.48 g cm⁻³, *D*_x = 1.48 g cm⁻³, μ(Mo Kα) = 0.812 mm⁻¹. The X-ray intensity was measured with a crystal of dimensions 0.23 × 0.36 × 0.44 mm on a Rigaku automated four-circle diffractometer with Mo Kα radiation monochromated by a graphite plate. Among the total 7661 reflections (the *h*, *k*, *l* set), those with 2θ ≤ 60° were measured by the θ-2θ scan mode at a speed of 2° min⁻¹ in θ. Thus, 4327 intensities with |*F*_o| > 3σ(|*F*_o|) were obtained and used for structure analysis. The intensities were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen and hydrogen atoms, respectively. The minimized function was *R*_w(*F*) = [Σw(|*F*_o| - |*F*_c|)|*F*_o|²]/Σw|*F*_o|²]^{1/2}, where the weight was calculated by w⁻¹ = [σ(|*F*_o|)]² + (0.015|*F*_o|)². Among 52 hydrogen atoms, the locations of 27 atoms were found by difference syntheses and those of the others estimated by calculations.

The structure was disordered. There were three possible positions for the methyl C atom in the propylenediamine moiety of *R*-dqpn.

- (1) Government Industrial Research Institute, Tohoku, Haranomachi, Sendai 983, Japan.
- (2) Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi-3, Kohoku-ku, Yokohama 223, Japan.
- (3) Institute for Solid State Physics, University of Tokyo, Roppongi-7, Minatoku, Tokyo 106, Japan.
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Table I. Elemental Analyses of the Complexes^a

complex perchlorate	% found (% calcd)			
	C	H	N	Cl
[Co(acac)(dqen')] ₂ ClO ₄	52.90 (52.56)	4.47 (4.41)	9.30 (9.79)	5.86 (6.22)
[Co(acac)(R-dqpn')] ₂ ClO ₄	53.43 (53.38)	4.82 (4.78)	8.97 (9.37)	5.87 (6.07)
[Co(acac)(R,R-dqchxn')] ₂ ClO ₄	54.26 (54.14)	5.34 (5.13)	8.96 (8.70)	5.54 (5.69)

^a For ligand abbreviations, see Figure 1.**Figure 1.** Structures and abbreviations of ligands (deprotonated species are expressed by primes: dqen', dqpn', and dqchxn').

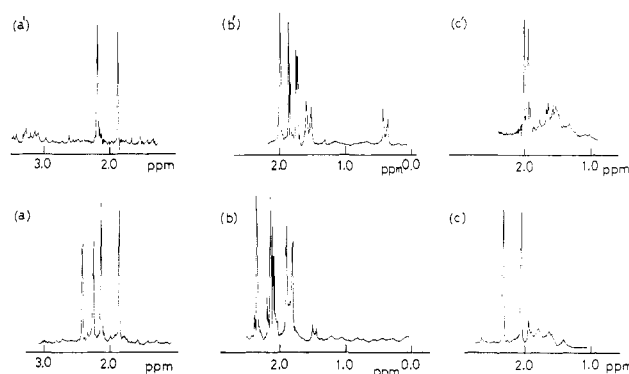
The weight for these was estimated by the trial and error method so that the isotropic thermal parameter (ca. 5.5 \AA^2) became nearly equal. The population parameters for C(C10)1, C(C10)2, C(C11), C(C10), C(C01)1, and C(C01)2 are 0.18, 0.41, 0.41, 0.18, 0.45, and 0.37, respectively, where the atom notation is shown in Figure 8. The final $R(F)$ and $R_w(F)$ values are 0.057 and 0.067, respectively. The positional and the equivalent isotropic thermal parameters are listed in Table II. The absolute configuration of the complex cations was determined on the basis of the known absolute configuration of *R*-dqpn. The separately refined enantiomeric structure gave the same R factors as those of the original structure because the crystal structure has approximately the center of inversion.

The calculation was performed by a FACOM 230-48 and a FACOM M-160F computer at the Institute for Solid State Physics, University of Tokyo, with the Universal Crystallographic Computation Program System UNICS III.¹⁹

Measurements. The pK_a values of the coordinated secondary amine in the complexes were determined spectroscopically in ethanol, i.e., by the analysis of the absorbance at 500 nm vs. acid concentration curves. The visible and ultraviolet absorption, CD, and ^1H NMR spectra were recorded with a Shimadzu Double 40-R spectrophotometer, a Jasco J-20 spectropolarimeter, and a JEOL FX-100 spectrometer, respectively, at room temperature.

Results

Preparation of the Complexes. Several attempts to prepare cobalt(III) complexes with the dqdm ligands were unsuccessful in aqueous solution. Reaction of tris(acetylacetonato)cobalt(III) with these ligands in a mixture of benzene and ethanol, however, gave an intense purple solution, from which black or dark purple diamagnetic complexes were isolated as perchlorates. The analytical data given in Table I conform to those for salts consisting of univalent cations and per-

**Figure 2.** ^1H NMR spectra of (a') [Co(acac)(dqen')]₂ClO₄, (b') [Co(acac)(R-dqpn')]₂ClO₄, and (c') [Co(acac)(R,R-dqchxn')]₂ClO₄. (a), (b), and (c) are the analogous spectra measured in 12 M DCl.

chlorate. Since the central metal ion of all the complexes is diamagnetic cobalt(III), the quadridentate ligand must coordinate in the deprotonated form, [Co(acac)(dqdm')]⁺. The corresponding parent complexes with neutral ligands were readily formed on addition of acid in organic solvents but isolated with difficulty.

NMR Spectra. The proton magnetic resonance signals of all the isolated complexes with both neutral and deprotonated quadridentate ligands were recorded in 12 M DCl and acetone- d_6 , respectively (Figure 2). All the complexes gave two sharp singlet peaks due to the acac⁻ chelate moiety at about 2.0 ppm, indicating that the complexes have cis- β geometry in which the two methyl groups of acetylacetonate are non-equivalent. Two kinds of doublets ($J = 6.7 \text{ Hz}$) with an intensity ratio 5:4 were observed around 1.6 and 0.4 ppm for the *R*-dqpn complex in deprotonated form. These two peaks can be assigned to the methyl groups on the (*R*)-propylenediamine chelate moiety. When the complex was dissolved in acid solution, the spectral feature in the methyl region changed remarkably; i.e., the methyl peaks at 0.4 ppm disappear while two methyl doublets appear at 1.80 and 1.44 ppm with the area ratio approximately 5:1. Thus, the peaks at 0.4 ppm in the basic solution must be assigned to the methyl group adjacent to the amide nitrogen.

Absorption and CD Spectra. The absorption and CD spectra are shown in Figures 3–5, and their numerical data are summarized in Table III. Both absorption and CD spectra of the present complexes exhibit striking changes depending on the pH of the solution. The spectra measured in ethanol correspond to those of the complexes with deprotonated ligand, while those measured in ethanol saturated with hydrogen chloride correspond to those of the complexes with neutral ligands. All the deprotonated complexes show two intense absorption bands ($\log \epsilon \approx 3.0\text{--}3.5$) in the visible region. The band shape and intensities are not similar to the normal d–d transition bands of cobalt(III) complexes. On the other hand, the spectra of the complexes with neutral ligands in the same region have a single absorption band and their intensities are much less. The bands are assigned to the first d–d bands on the basis of the peak location and intensity. A remarkable spectral change due to protonation and deprotonation of the coordinated ligand was also observed in the ultraviolet region

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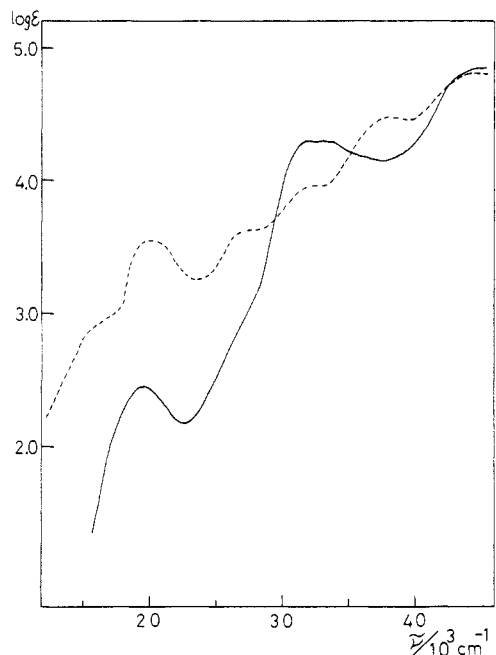


Figure 3. Absorption spectra of $[\text{Co}(\text{acac})(\text{dqen}')]\text{ClO}_4$ in ethanol saturated with HCl (—) and in ethanol (---).

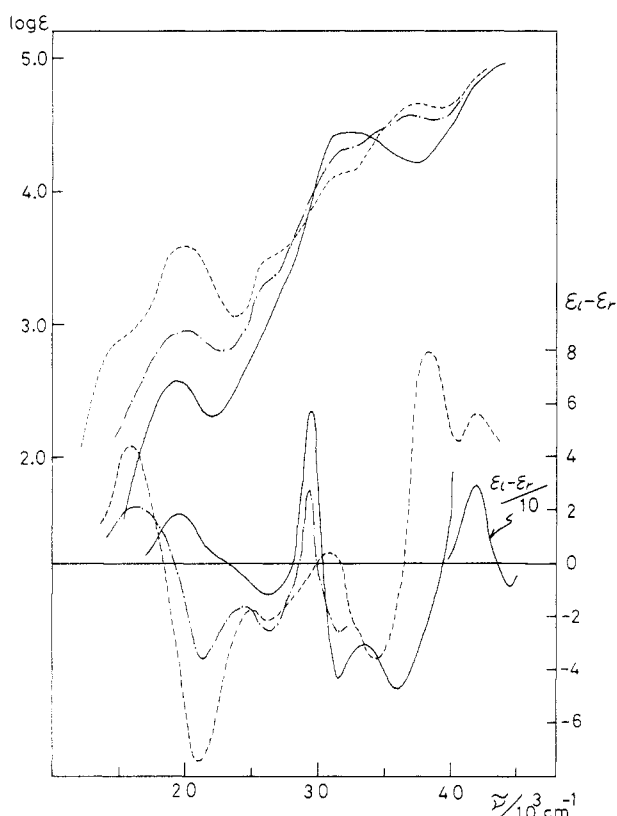


Figure 4. Absorption and CD spectra of $[\text{Co}(\text{acac})(R\text{-dqpn}')]\text{ClO}_4$ in ethanol saturated with HCl (—) and in ethanol (---) and intermediate spectra (-·-).

where the ligand $\pi-\pi^*$ absorption is predominant.

The remarkable change in the absorption spectra is accompanied by the change in CD over the whole wavelength region. The complexes with deprotonated ligands ($R\text{-dqpn}'$ and $R,R\text{-dqchxn}'$) give intense CD peaks, positive and negative from longer to shorter wavelength, in the visible region. The CD pattern remarkably changes on dissolution in acid media. The $R\text{-dqpn}$ complex gives a single positive peak, and the $R,R\text{-dqchxn}$ gives small negative peaks in the d-d transition

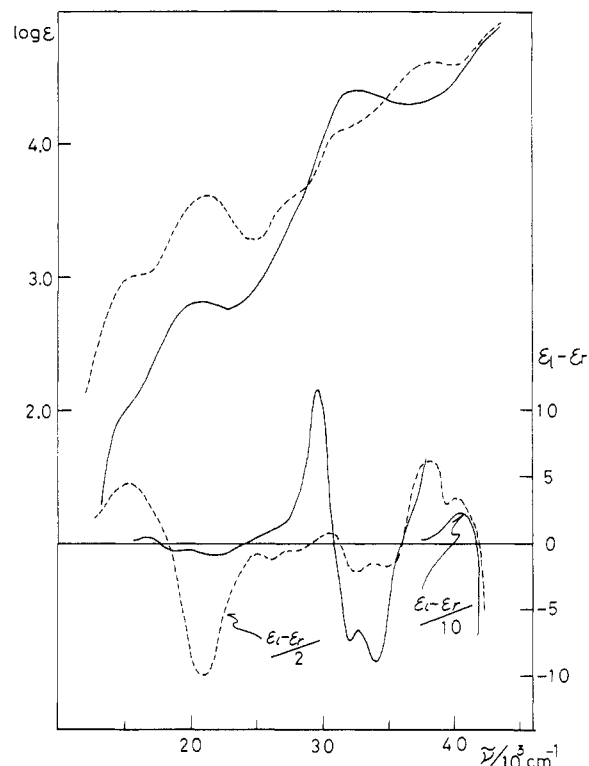


Figure 5. Absorption and CD spectra of $[\text{Co}(\text{acac})(R,R\text{-dqchxn}')]\text{ClO}_4$ in ethanol saturated with HCl (—) and in ethanol (---).

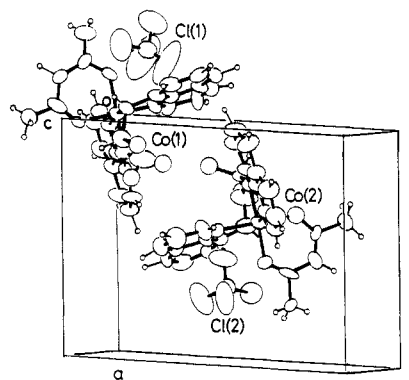


Figure 6. Unit cell structure of $[\text{Co}(\text{acac})(R\text{-dqpn}')]\text{ClO}_4$ projected approximately parallel to the c axis.

region. Both complexes show a sharp positive and a negative CD from longer to shorter wavelength around $30\,000\text{ cm}^{-1}$, which should correspond to the exciton splitting of the $\pi-\pi^*$ transition of the quinoline rings.²¹ Such clear exciton CD bands are not observed for the complexes with deprotonated ligands.

The spectrum gives a pattern intermediate between those of the protonated and the deprotonated $R\text{-dqpn}$ complex on careful adjustment of pH (Figure 4). Isosbestic points are seen in neither the absorption nor the CD spectra, indicating that several species other than those with the two limiting structures may be present in the solution.

Crystal Structure of $[\text{Co}(\text{acac})(R\text{-dqpn}')]\text{ClO}_4$. Figure 6 shows the crystal structure projected approximately parallel to the c axis. There are two crystallographically independent complex cations and two perchlorate ions in the unit cell. Perspective drawings of the two complex cations are given in Figure 7. The absolute configurations of complexes 1 and 2 are Δ and Λ , respectively. The quadridentate ligand $R\text{-dqpn}'$

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Table II. Positional Parameters ($\times 10^4$; for H, $\times 10^3$) and Equivalent Isotropic Thermal Parameters

atom	x	y	z	$B_{eq}, \text{\AA}^2$	atom	x	y	z	$B_{eq}, \text{\AA}^2$
Cl(1)	6793 (2)	5364 (2)	7725 (3)	5.7 (0.1)	C(013)	4946 (11)	2928 (10)	4336 (11)	6.9 (0.4)
O(11)	6974 (7)	6062 (7)	6880 (9)	8.8 (0.4)	C(014)	5391 (10)	2152 (7)	3184 (17)	8.5 (0.5)
O(12)	7337 (11)	4311 (8)	6947 (9)	11.8 (0.4)	C(015)	5520 (7)	2391 (6)	1614 (10)	4.3 (0.3)
O(13)	5549 (8)	5271 (11)	7820 (15)	13.7 (0.6)	C(016)	5050 (7)	3422 (6)	1553 (11)	4.5 (0.3)
O(14)	7182 (11)	5565 (6)	9166 (10)	11.5 (0.4)	C(017)	5002 (7)	3726 (6)	325 (9)	3.7 (0.2)
Cl(2)	-2604 (2)	120 (2)	-5162 (3)	5.8 (0.1)	C(018)	5567 (8)	3075 (7)	-982 (11)	5.3 (0.3)
O(21)	-2210 (17)	-295 (11)	-6537 (12)	21.7 (0.9)	C(019)	6145 (9)	2115 (8)	-971 (10)	6.0 (0.3)
O(22)	-2124 (18)	914 (10)	-4605 (14)	20.0 (0.9)	C(020)	6043 (7)	1792 (6)	299 (12)	5.2 (0.4)
O(23)	-3764 (12)	275 (14)	-5402 (24)	20.9 (1.1)	C(021)	7513 (9)	6768 (8)	3339 (17)	7.8 (0.5)
O(24)	-2767 (13)	-693 (9)	-4537 (15)	14.6 (0.6)	C(022)	6176 (7)	6627 (7)	2866 (9)	4.5 (0.3)
Co(1)	0	0	0	3.6 (0.1)	C(023)	5574 (8)	7525 (7)	2648 (11)	4.9 (0.3)
O(1)	-1643 (5)	-281 (4)	-276 (7)	4.6 (0.2)	C(024)	4444 (7)	7454 (6)	2059 (9)	3.8 (0.3)
O(2)	447 (4)	-1246 (4)	593 (6)	4.0 (0.2)	C(025)	3904 (9)	8432 (8)	1701 (12)	5.8 (0.4)
N(1)	577 (6)	-675 (5)	-2026 (7)	3.9 (0.2)	C(C10)1 ^a	2590 (50)	911 (43)	2034 (62)	5.6 (1.2)
N(2)	1613 (6)	307 (6)	340 (8)	4.2 (0.2)	C(C10)2 ^a	1916 (22)	2029 (19)	1972 (28)	5.5 (0.5)
N(3)	-337 (6)	775 (5)	2160 (7)	4.0 (0.2)	C(C11) ^a	1108 (21)	1596 (19)	4466 (27)	5.5 (0.5)
N(4)	-418 (6)	1273 (5)	-397 (8)	4.2 (0.2)	C(C010) ^a	1952 (49)	3417 (43)	665 (62)	5.5 (1.2)
C(1)	56 (8)	-1232 (8)	-3200 (11)	5.0 (0.3)	C(C011)1 ^a	2903 (20)	5013 (17)	-1157 (24)	5.4 (0.5)
C(2)	539 (9)	-1653 (8)	-4561 (9)	5.5 (0.3)	C(C011)2 ^a	3029 (24)	4072 (21)	-1821 (30)	5.4 (0.6)
C(3)	1717 (9)	-1452 (9)	-4795 (10)	6.1 (0.3)	H(N3)	-78 (7)	43 (6)	259 (8)	4.4 (1.8)
C(4)	2361 (8)	-877 (7)	-3654 (10)	4.4 (0.3)	H(C1)	-73 (7)	-135 (6)	-279 (8)	4.6 (1.9)
C(5)	1769 (6)	-477 (6)	-2259 (8)	3.4 (0.2)	H(C2)	22 (6)	-232 (6)	-528 (8)	4.0 (1.7)
C(6)	2332 (7)	106 (6)	-942 (10)	3.9 (0.2)	H(C3)	206 (8)	-192 (7)	-578 (10)	6.5 (2.2)
C(7)	3516 (7)	313 (8)	-1120 (11)	5.3 (0.3)	H(C7)	379 (6)	73 (5)	-27 (8)	3.6 (1.6)
C(8)	4100 (8)	-77 (8)	-2674 (12)	6.0 (0.4)	H(C8)	501 (6)	14 (6)	-299 (8)	4.1 (1.7)
C(9)	3571 (8)	-595 (10)	-3800 (11)	6.8 (0.4)	H(C9)	402 (8)	-85 (7)	-480 (10)	6.5 (2.2)
C(10)	1794 (11)	1235 (12)	1650 (14)	8.9 (0.6)	H(C11)	138 (6)	2 (5)	288 (7)	3.6 (1.6)
C(11)	944 (9)	733 (8)	2806 (9)	5.1 (0.3)	H(C12)	-4 (6)	98 (5)	-250 (7)	3.1 (1.5)
C(12)	-389 (10)	1510 (8)	-1740 (12)	5.8 (0.3)	H(C13)	-62 (7)	260 (6)	-309 (9)	5.8 (2.1)
C(13)	-776 (12)	2501 (8)	-1959 (16)	8.3 (0.5)	H(C14)	-145 (7)	395 (6)	-71 (9)	5.5 (2.0)
C(14)	-1312 (9)	3232 (9)	-689 (14)	7.1 (0.4)	H(C18)	-143 (7)	256 (6)	447 (9)	5.5 (2.0)
C(15)	-1374 (7)	3065 (7)	487 (13)	6.1 (0.3)	H(C19)	-241 (8)	414 (7)	399 (10)	7.0 (2.4)
C(16)	-866 (7)	2090 (6)	734 (8)	3.6 (0.2)	H(C20)	-234 (8)	465 (7)	175 (10)	6.6 (2.2)
C(17)	-942 (7)	1871 (7)	2179 (11)	5.1 (0.3)	H(C21)1	-357 (6)	-173 (5)	-69 (7)	3.3 (1.5)
C(18)	-1493 (8)	2590 (8)	3341 (11)	6.3 (0.3)	H(C21)2	-383 (8)	-94 (7)	-31 (10)	7.4 (2.5)
C(19)	-1962 (9)	3557 (7)	3124 (17)	9.1 (0.5)	H(C21)3	-331 (7)	-115 (6)	-190 (9)	6.1 (2.2)
C(20)	-1937 (8)	3884 (7)	1842 (15)	7.2 (0.5)	H(C23)	-182 (7)	-266 (6)	21 (9)	5.7 (2.1)
C(21)	-3291 (9)	-1234 (9)	-810 (12)	6.4 (0.3)	H(C25)1	2 (7)	-361 (6)	36 (8)	4.7 (1.9)
C(22)	-2112 (8)	-1179 (6)	-374 (10)	4.6 (0.3)	H(C25)2	124 (8)	-319 (7)	52 (10)	6.9 (2.4)
C(23)	-1422 (7)	-1963 (6)	105 (9)	4.2 (0.3)	H(C25)3	55 (8)	-263 (6)	224 (9)	6.3 (2.2)
C(24)	-201 (8)	-1998 (8)	511 (9)	5.0 (0.3)	H(N03)	490 (7)	505 (6)	-16 (9)	5.6 (2.0)
C(25)	346 (8)	-2892 (7)	1064 (10)	4.9 (0.3)	H(C01)	495 (6)	676 (6)	553 (8)	4.1 (1.7)
Co(2)	4145 (1)	5493 (1)	2513 (1)	3.5 (0.1)	H(C02)	414 (7)	745 (6)	821 (9)	4.9 (1.9)
O(01)	5794 (5)	5786 (4)	2869 (6)	3.8 (0.2)	H(C03)	217 (8)	716 (7)	858 (10)	7.1 (2.4)
O(02)	3741 (6)	6726 (5)	1930 (7)	5.3 (0.2)	H(C07)	36 (8)	443 (7)	290 (9)	6.3 (2.2)
N(01)	3580 (6)	6153 (5)	4583 (7)	3.9 (0.2)	H(C08)	-62 (8)	483 (7)	505 (9)	6.5 (2.3)
N(02)	2546 (6)	5128 (5)	2285 (7)	3.6 (0.2)	H(C09)	28 (6)	620 (5)	772 (7)	2.8 (1.4)
N(03)	4386 (7)	4661 (7)	429 (8)	5.6 (0.2)	H(C010)	140 (7)	478 (6)	44 (9)	5.1 (1.9)
N(04)	4555 (6)	4134 (5)	2985 (7)	3.8 (0.2)	H(C012)	437 (6)	441 (6)	506 (8)	4.4 (1.8)
C(01)	4229 (7)	6718 (7)	5687 (9)	4.7 (0.2)	H(C013)	481 (7)	261 (6)	517 (8)	4.5 (1.8)
C(02)	3655 (10)	7045 (9)	7221 (11)	6.4 (0.3)	H(C014)	589 (8)	155 (7)	343 (10)	6.6 (2.3)
C(03)	2532 (10)	6841 (9)	7469 (11)	6.6 (0.3)	H(C018)	557 (7)	336 (6)	-198 (9)	5.3 (2.0)
C(04)	1901 (8)	6175 (8)	6295 (11)	5.4 (0.3)	H(C019)	634 (7)	173 (6)	-161 (9)	4.8 (1.8)
C(05)	2467 (8)	5920 (8)	4797 (11)	5.0 (0.3)	H(C020)	639 (8)	102 (7)	25 (10)	6.4 (2.2)
C(06)	1907 (7)	5309 (7)	3567 (10)	4.5 (0.3)	H(C021)1	774 (8)	735 (7)	340 (10)	6.9 (2.4)
C(07)	785 (8)	4938 (9)	3803 (11)	5.6 (0.3)	H(C021)2	784 (6)	631 (6)	376 (8)	4.1 (1.7)
C(08)	203 (8)	5217 (9)	5100 (12)	6.5 (0.4)	H(C021)3	812 (9)	633 (8)	230 (11)	8.8 (2.8)
C(09)	709 (10)	5938 (9)	6504 (15)	7.9 (0.4)	H(C023)	596 (8)	824 (7)	295 (10)	6.1 (2.2)
C(010)	2290 (6)	4512 (6)	815 (8)	3.1 (0.2)	H(C025)1	327 (7)	822 (6)	115 (9)	5.5 (2.0)
C(011)	3216 (10)	4450 (12)	-348 (12)	8.2 (0.4)	H(C025)2	450 (7)	891 (6)	132 (9)	5.2 (2.0)
C(012)	4538 (10)	3885 (8)	4237 (11)	5.7 (0.3)	H(C025)3	312 (8)	877 (7)	251 (10)	7.5 (2.5)

^a Population parameters of the disordered methyl C atoms: C(C10)1, 0.18; C(C10)2, 0.41; C(C11), 0.41; C(C010), 0.18; C(C011)1, 0.45; C(C011)2, 0.37.

is coordinated to the Co^{III} ions in cis- β form in both cations. The observed electron density distribution was not reasonably interpreted without taking structural disorder into account. Edge-on views of the central chelate rings of cations **1** and **2** are shown in Figure 8.

The hatched spheres in the figures denote the possible locations of disordered methyl C atoms. Two of them are attached to C(10) and one to C(11) of complex **1**, whereas two are bonded to C(011) and one to C(010) of complex **2**. The isotropic thermal parameters of C(10) and C(011) are 8.9 and

8.2 \AA^2 , respectively. On the other hand, those of C(11) and C(010) are 5.1 and 3.1 \AA^2 , respectively. The relatively large values for the former suggest the positional disorder of C(10) and C(011) atoms, which is related to the orientation of the disordered methyl groups on them. There is an overall trend that the nitrogen β to the methyl group in the (*R*)-propylenediamine moiety is preferentially deprotonated over the α -nitrogen by a factor of 1.5.

The bond distances and angles within the (*R*)-propylenediamine chelate moieties of complexes **1** and **2** are listed in

Table III. Absorption (AB) and Circular Dichroism (CD) Spectral Data

complex	solvent	AB $10^{-3}\tilde{\nu}$, cm^{-1} (log ϵ)	CD $10^{-3}\tilde{\nu}$, cm^{-1} ($\epsilon_1 - \epsilon_2$)
[Co(acac)(dqen)] ²⁺	ethanol-HCl ^a	19.80 (2.45)	
		31.64 (4.27)	
		32.79 (4.27)	
		44.64 (4.85)	
		15.63 sh ^b (2.84)	
[Co(acac)(dqen')] ⁺	ethanol	20.20 (3.53)	
		27.03 (3.60)	
		31.75 sh (3.94)	
		37.31 (4.43)	
		44.25 (4.72)	
[Co(acac)(R-dqpn)] ²⁺	ethanol-HCl	19.61 (2.53)	19.15 (+1.74)
			26.18 (-1.35)
		31.65 (4.38)	29.15 (+5.85)
		32.79 (4.38)	30.86 (-4.30)
			35.71 (-4.30)
[Co(acac)(R-dqpn')] ⁺	ethanol	43.67 (4.60)	41.67 (+2.93)
		15.38 (2.88)	15.87 (+4.30)
		20.20 (3.56)	21.05 (-7.38)
		27.03 (3.50)	
		31.75 sh (4.08)	34.01 (-3.61)
[Co(acac)(R,R-dqchxn)] ²⁺	ethanol-HCl	37.31 (4.56)	37.88 (+7.90)
		44.64 (5.20)	42.02 (+6.20)
		14.93 sh (1.94)	17.24 (+0.28)
		20.41 (2.78)	19.42 (-0.40)
			22.22 (-0.50)
[Co(acac)(R,R-dqchxn')] ⁺	ethanol		25.00 sh (+0.48)
		31.75 (4.34)	29.41 (+11.6)
		32.47 (4.34)	32.05 (-6.60)
		35.09 sh (4.29)	34.48 (-9.00)
		43.10 (4.87)	40.00 (+24.6)
		15.63 (3.00)	15.87 (+8.50)
		20.66 (3.56)	21.05 (-19.7)
		26.66 sh (3.56)	30.49 (+1.50)
		31.75 sh (4.11)	32.26 (-3.78)
			34.97 (-3.40)
			37.59 (+13.2)
		37.74 (4.55)	40.65 (+9.50)
		44.25 (4.92)	42.74 (-4.30)

^a Ethanol saturated with HCl. ^b sh = shoulder band.

Table IV. The bond distances involving the disordered methyl carbons are irregular; i.e., those on C(10) and C(011) are too short, while those on C(11) and C(010) are too long. This fact is due to the improper position of C atoms in the five-membered rings and is more marked in complex 1. The long C(10)–C(11) distance (1.71 Å) seems to be due to the error introduced by the high correlation of the parameter with the large thermal motion of the C(10) atom, which also brings about the conformational change of the chelate ring.

For the same reason, the distorted bond angle N(2)–C(10)–C(11) (90.7°) is not significant.

The sums of the three bond angles around the N atoms N(2) and N(02) in complexes 1 and 2, respectively, are 347 and 358°. These values suggest sp² hybridization, and these two N atoms seem to be deprotonated. They are the secondary N atoms shared by the two meridionally linked chelate rings. On the other hand, the sums of the three bond angles around N(3) (in complex 1) and N(03) (in complex 2) are 322 and 333°, respectively, and hydrogen atoms on them are found on a difference-density map. Each of them is shared by two five-membered rings, which are facial to each other. The mean value of Co–N(2) and Co–N(02) distances is 1.879 (7) Å, which is shorter by 0.1 Å than that of Co–N(3) and Co–N(03), suggesting an increased covalency between Co and –N–.

Discussion

Deprotonation of Coordinated Quinolyamines. Cobalt(III) complexes with deprotonated amines have been synthesized with the following types of ligands: (i) Schiff bases formed between *o*-aminobenzaldehyde and ammonia²² or propylene-

Table IV. Bond Lengths (Å) and Angles (deg) within the Central Chelate Rings of Complexes 1 and 2

	1	2
Co–N(2)	1.881 (6)	1.877 (7)
Co–N(3)	1.996 (6)	1.946 (7)
N(2)–C(10)	1.503 (14)	1.429 (9)
N(3)–C(11)	1.560 (12)	1.508 (13)
C(10)–C(11)	1.712 (18)	1.455 (13)
C(10)–C(C10)1	1.07 (6)	
C(10)–C(C10)2	1.04 (3)	
C(11)–C(C11)	1.67 (2)	
C(010)–C(C010)		1.50 (6)
C(011)–C(C011)1		1.24 (3)
C(011)–C(C011)2		1.35 (3)
N(2)–Co–N(3)	85.9 (3)	84.4 (3)
Co–N(2)–C(6)	114.1 (5)	114.1 (5)
Co–N(2)–C(10)	115.5 (6)	114.9 (5)
C(6)–N(2)–C(10)	120.2 (8)	129.6 (7)
Co–N(3)–C(11)	101.8 (4)	112.8 (6)
Co–N(3)–C(17)	106.0 (5)	111.0 (6)
C(11)–N(3)–C(17)	117.6 (6)	108.1 (9)
N(2)–C(10)–C(11)	90.7 (9)	115.3 (7)
N(3)–C(11)–C(10)	102.5 (8)	106.8 (8)

diamine,²² (ii) aromatic *o*-diamines, e.g., *o*-phenylenediamine,²³ and (iii) some oligopeptides including biuret.²⁴ There seems to be a common feature among these ligands that the basicity

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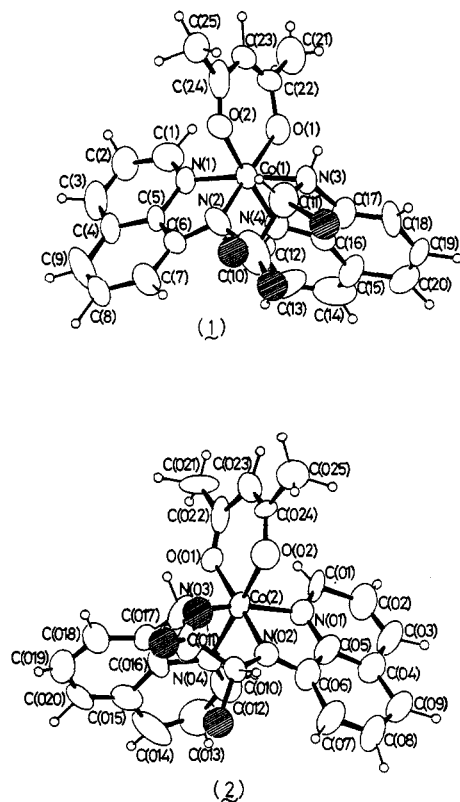


Figure 7. Perspective drawings of the complex cations Δ -[Co(acac)(*R*-dqpn')]⁺ (1) and Λ -[Co(acac)(*R*-dqpn')]⁺ (2). The hatched carbon atoms denote the disordered methyl carbons.

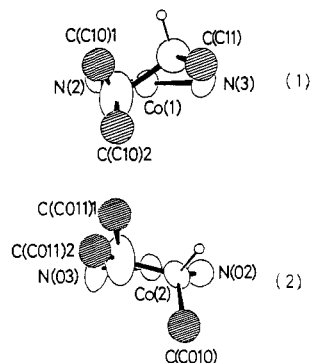


Figure 8. Edge-on views of the central chelate moiety of [Co(acac)(*R*-dqpn')]⁺ (1, Δ -isomer; 2, Λ -isomer).

of the amine nitrogen is low. This fact is presumably due to the electron-withdrawing character of the remaining moiety (substituted phenyl and adjacent carbonyl) of the ligands. 8-Aminoquinoline also has a smaller pK_a (4.04) than those of 2-aminopyridine (6.71) and ethylenediamine (6.17).²⁵ Spectroscopy of the present complexes with dqen, *R*-dqpn, and *R,R*-dqchxn at 500 nm gave apparent pK_a values of the coordinated amino nitrogen of 3.65, 3.66, and 3.84, respectively. Facile formation of such deprotonated complexes may be attributed to the low basicity of the amino nitrogens directly attached to the quinolyl ring. Curry and Busch discussed that deprotonation of nitrogen in a carbon chain of a sexidentate ligand in an iron(II) complex favors a meridional structure.²⁶ Our complexes also have the *cis*- β configuration in which three of the nitrogen atoms, including the deprotonated nitrogen, are meridional to one another.

The striking change in the visible absorption spectra between the complexes with deprotonated and neutral ligands cannot be explained by the change in the number of lone-pair electrons on the ligating atom. The aromatic ring moieties assume anion-radical character on deprotonation, and the negative charge may be delocalized in the aromatic ring to facilitate the charge transfer to the cobalt(III) ion. The change in the ultraviolet spectra on the deprotonation of a secondary amine can also be explained by the change of electronic state of the aromatic ring. When the proton is on the secondary amine, the intensity of the visible absorption band decreases and becomes characteristic of the first d-d transition band of the [Co^{III}N₄O₂] chromophore.

Selectivity in the Formation of Deprotonated [Co(acac)(*R*-dqpn')ClO₄]. X-ray crystallographic analysis of [Co(acac)(*R*-dqpn')ClO₄] containing deprotonated *R*-dqpn' disclosed that both Δ - and Λ -isomers are contained in the unit cell. Each isomer consists of two geometrical isomers in which the nitrogen either α or β to the asymmetric carbon is deprotonated. Positional disorder at the chelate ring of the propylenediamine moiety suggests that the α -amide form of the Δ -isomer consists of both δ - and λ -conformers and the β -amide form of only the λ -conformer. On the other hand, the β -amide form of the Λ -isomer contains two conformers and the α -amide form only δ -conformer. The crystalline complex contains equal amounts of Δ - and Λ -isomers. However, this fact does not necessarily indicate that they are equally present in ethanol solution. The CD strength of the ethanol solution of [Co(acac)(*R*-dqpn')]⁺ in the visible region is larger than that of the vicinal effect of ordinary cobalt(III) complexes containing optically active amines. However, the extinction coefficients of the absorption peaks corresponding to the CD peaks are also very large in the visible region so that the contribution of configurational effect to the CD pattern is uncertain. Nevertheless, the selectivity in forming a Δ - or Λ -isomer of the deprotonated ligand *R*-dqpn' can be significantly smaller than that of the protonated ligand since the exciton CD strength is very weak as compared with that in acid solution (vide infra). The ¹H NMR spectrum of this complex in deuterated acetone gives two methyl doublets at ca. 0.4 and 1.6 ppm. The location of the former is at an unusually high-field region, and it disappears on addition of hydrogen chloride. Hence, this doublet should be due to the methyl group adjacent to the deprotonated nitrogen. If the equatorial and axial methyl groups of the Δ -isomer are fixed in the ethanolic solution as in the solid state, two sets of doublets should appear around 0.4 ppm. Since the observed signals are sharp, it is unlikely that both axial and equatorial methyl protons give accidentally equal chemical shifts. Hence, the interconversion between the δ - and the λ -conformers should be taking place in the solution at room temperature. Puckering of the central chelate ring of a linear quadridentate ligand usually brings about substantial difference of the chelate rings. However, under the given condition where one of the secondary amine protons is deprotonated, the puckering can take place without great strain. The strength of the two doublets at 0.4 and 1.6 ppm has a ratio of 4:5. Hence, the amino nitrogen β to the asymmetric carbon is slightly more easily deprotonated than that α to the asymmetric carbon. This fact is rather in good accord with the fact that the nitrogen β to the asymmetric carbon is preferentially deprotonated over the α -nitrogen by a factor of 1.5 in the crystalline state.

[Co(acac)(*R*-dqpn)]²⁺. Attempts to crystallize the complex containing neutral dqpn were unsuccessful, and the discussion is limited to the solution data. No information was obtained concerning the geometrical isomerism involving the location of the methyl group on one of the methylene carbons, since such a difference in location does not seem to bring about

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different chemical shifts on the ^1H NMR signal. The methyl proton on the propylenediamine moiety gives two signals at 1.44 and 1.80 ppm, and their intensity ratio is ca. 1:5. The signals at 1.44 and 1.80 ppm are assigned to equatorial and axial methyl protons, respectively. Since equatorial orientation of methyl group in the λ -gauche conformer is considered to involve less steric hindrance than the axial orientation in the δ -gauche conformer, the former must preferentially be formed by a factor of ca. 5.

The characteristic exciton CD peaks associated with the ligand π - π^* transition suggest that the R -dqpn complex takes the Λ -configuration preferentially. Appearance of a single positive peak with $\Delta\epsilon \simeq 2$ in the first d-d transition region is also consistent with the Λ -configuration.²⁷ Since the change of the CD pattern takes place swiftly and reversibly on addition of hydrogen chloride and sodium ethoxide to the ethanol solution of $[\text{Co}(\text{acac})(R\text{-dqpn})]^+$, a rapid rearrangement of the quadridentate ligand should take place, associated with the protonation and deprotonation of the ligand. Mere protonation and deprotonation in situ are not sufficient for the structure to change between $[\text{Co}(\text{acac})(R\text{-dqpn})]^+$ and $[\text{Co}(\text{acac})(R\text{-dqpn})]^{2+}$; e.g., the Co-N(quinolyl) bond should be broken and re-formed simultaneously at a different coordination site. Ligand substitution reactions of cobalt(III) complexes are accelerated by the formation of conjugate bases in basic solution. Since one of the amino nitrogens of the present complex is completely deprotonated in ethanolic solution, the labile substitution of the dqpn ligand in the present complex can be easily understood. The CD spectrum involves many kinds of contributions including configurational and conformational and of ligating and remote asymmetric atoms. The change in their contribution can take place at different rates on addition of hydrogen chloride or sodium ethoxide. Hence the absence of an isosbestic point on the CD patterns does not seem unusual.

CD and Stereochemistry of Deprotonated $[\text{Co}(\text{acac})(R,R\text{-dqchxn})]^+$ and $[\text{Co}(\text{acac})(R,R\text{-dqchxn})]^{2+}$. The CD pattern

of the deprotonated R,R -dqchxn complex is very similar to that of the deprotonated R -dqpn complex over the entire wavelength region, while the peak strength of the former is 2 or 3 times that of the latter. The difference in the CD strength must be partly attributed to the difference in the number of asymmetric carbons in the ligand, which may additively contribute to the CD. In addition to this vicinal contribution, the chelate ring of the R,R -chxn moiety of the quadridentate ligand is uniquely restricted to λ -gauche conformation by the equatorial orientation of the two side branches. The conformational puckering of the R,R -chxn chelate should not take place even when the amine proton is deprotonated. Further, the fixed conformation of the R,R -chxn chelate should give rise to the stereoselective coordination of the dqchxn around the cobalt ion. Unfortunately, neither the absolute configuration of the preferentially formed complex nor the Δ : Λ ratio in solution is clear from the CD spectra because of lack of empirical information about the structure and CD of these types of complexes.

The absorption and CD spectra of the complex with neutral R,R -dqchxn gave the rather typical pattern for the $[\text{Co}^{\text{III}}\text{N}_4\text{O}_2]$ type complexes containing heteroaromatic ligands (2,2'-bipyridine or 1,10-phenanthroline). The complex gives sharp exciton CD peaks associated with ligand π - π^* transitions of the quinoline rings. The absolute configuration can be assigned to Λ on the basis of the theoretical prediction.²¹ However the complex gives weak negative peaks in the first d-d transition region, which is inconsistent with the prediction from the exciton CD. Molecular model studies suggest that this complex has a rather large stress in the quadridentate ligand, which may result in change of CD pattern.

Registry No. $[\text{Co}(\text{acac})(\text{dqn}')]\text{ClO}_4$, 85735-57-5; $[\text{Co}(\text{acac})(R\text{-dqpn}')]\text{ClO}_4$, 85735-59-7; $[\text{Co}(\text{acac})(R,R\text{-dqchxn}')]\text{ClO}_4$, 85735-61-1; $[\text{Co}(\text{acac})(\text{dqn})]^{2+}$, 85735-62-2; $[\text{Co}(\text{acac})(R\text{-dqpn})]^{2+}$, 85735-63-3; $[\text{Co}(\text{acac})(R,R\text{-dqchxn})]^{2+}$, 85735-64-4.

Supplementary Material Available: Tables of thermal parameters, bond lengths, bond angles, and structure factors for $\text{Co}(\text{acac})(\text{dqpn})$ (28 pages). Ordering information is given on any current masthead page.

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