β-Keto Amino Enolates Binding to Transition Metals: Synthesis and Structure of the Ion-Pair Form and Its Mono- and Bidentate Coordination to Zirconium and Nickel

Pier Giorgio Cozzi, Patrick Veya, and Carlo Floriani*

Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

Angiola Chiesi-Villa and Corrado Rizzoli

Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy

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Summary: The 2-piperidinoacetophenone, 1, was deprotonated in THF by KH, and the resulting β-keto amino enolate–potassium ion pair, 2, complexed with 18-crown-6 to give 3, in which the enolate group chelates the [K(18-crown-6)]⁺ moiety. The reaction of 2 with cp_2ZrCl_2 [cp = η^5-C_5H_5] afforded complex 4 in which the β-keto amino enolate exhibits an η^1-O bonding mode to zirconium(IV). The enolate 2 acts as a N–O bidentate ligand complexing Ni(II) in the form of a square planar, diamagnetic complex. Crystallographic details: 3 is monoclinic, space group $P2_1/n$, with a = 11.836(2) Å, b = 16.757(3) Å, c = 13.899(2) Å, β = 95.55(1)°, Z = 4, and R = 0.081; 5 is triclinic, space group $P\bar{1}$, with a = 9.415(1) Å, b = 11.533(1) Å, c = 17.892(3) Å, α = 102.81(2)°, β = 92.00(2)°, γ = 67.28(2)°, Z = 3, and R = 0.057.

Introduction

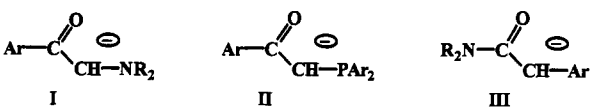
Amino functionalized monocyclic 2-azetidinones are important starting materials for the synthesis of β-lactam antibiotics.[1] The standard synthetic procedure for preparing the 2-aminoazetidinone is the condensation of metal amino enolates with aldehydes and imines.[2] The amino enolate moiety is also an important template for the synthesis of non-proteinogenic amino acids,[3] precursors of enzyme inhibitors and biologically active compounds.

The diastereocontrol in aldol condensation of amino enolates with aldehydes or imines occurs *via* intramolecular chelation with a Lewis acid.[4] The chelation with Lewis acids stabilizes the enolate and promotes the reaction with unactivated substrates; chelation is also responsible in some cases for a rate enhancement in reactions involving organometallic compounds.[5] Reactions of noncoordinating metal amino enolates with electrophiles give other diastereoisomers.[6] The use of transition metals in 2,3 dipolar cycloaddition of amino enolate reactions allows stereoselective control as a result of a rigid chelate transition state.[7]

In all the reactions reported, the transition metal complexes of β-keto amino enolates are employed to enhance the stereoselectivity of successive reactions. The use of β-keto amino enolates as ligands for transition metals in catalytic reactions has scarcely been considered.[8]

The β-keto amino enolate should parallel the corresponding β-keto phosphino enolate[9] in binding to transition metals, *i.e.* acting as an N,O bidentate ligand, and in reactivity. Two major differences to be expected are the nucleophilicity of the enolato carbon and the nature of the donor atoms binding to the transition metal. The latter property will clearly affect the electronic properties of the metal.

The transition metal assisted chemistry of the geometrical isomer, the amino enolate **III**, is largely known, and we have recently reported some of its interaction modes



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with transition metals.[10] The β-keto amino enolate functionality was, however, easily made chiral, expanding

* To whom correspondence should be addressed.

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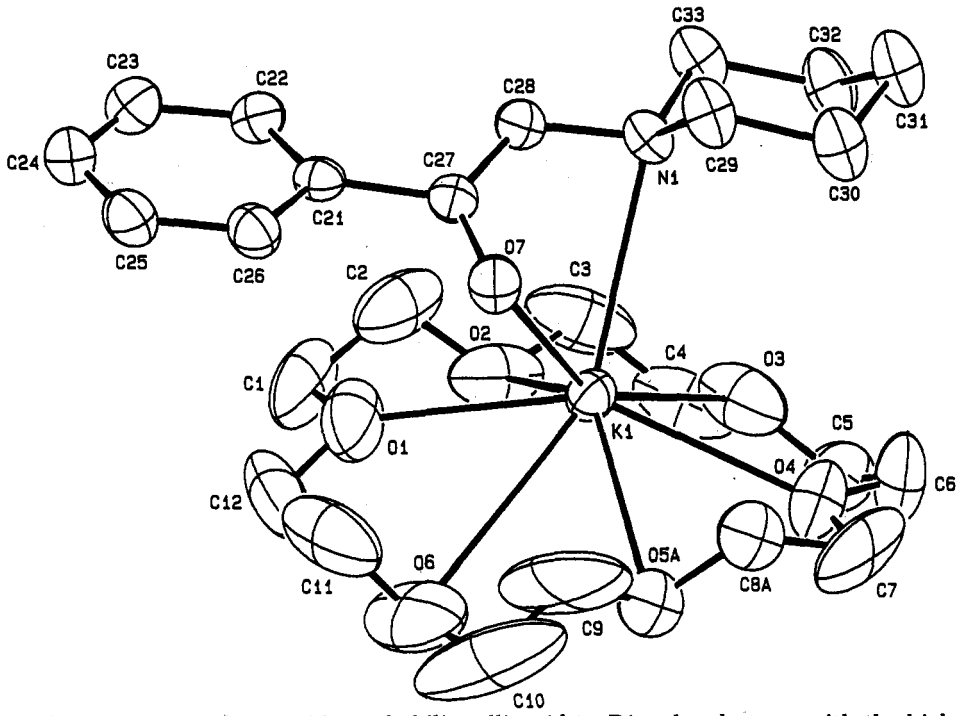
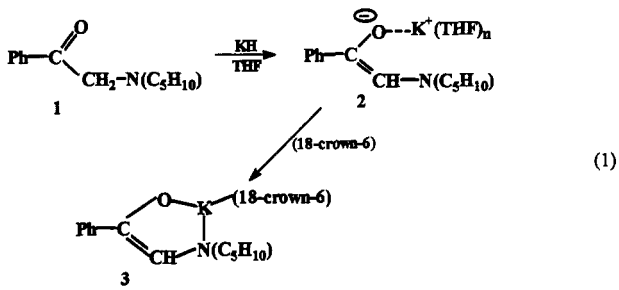


Figure 1. ORTEP drawing of complex 3 (30% probability ellipsoids). Disordered atoms with the highest site occupation factors have been included.

considerably the interest in catalytic reactions. This paper is devoted to the generation and isolation of the ion-pair form of 1 [Ar = Ph; R_2 = C_5H_{10}], its reaction with an oxophilic metal, and the corresponding binary complex with nickel(II).

Results and Discussion

The β-keto amino enolate 1 suitable for organometallic synthesis was generated *via* deprotonation of 1 with KH in THF. When deprotonation was followed by the addition of 18-crown-6, the ion-pair form 3 was isolated as a crystalline solid.



(1)

The full characterization of 3 includes a single crystal X-ray analysis, and its structure is shown in Figure 1, while selected bond distances and angles are listed in Table 4. The ^{1}H NMR spectrum shows the presence of a single diastereoisomer, very probably the *Z* one, as supported by the X-ray analysis and by the general finding that stereogenic acetophenones give preferential *Z* type enolization.[11] The crystal structure consists of discrete complex molecules of the *Z* diastereoisomer, where the keto amino enolate anion behaves as a bidentate ligand bonding to the K(18-crown-6) moiety through the O7 and N1 atoms. This preference in our case is enhanced by the intramolecular chelation to the potassium ion. The K–O7 distance [2.740(4) Å] is longer than that observed in analogous 18-crown-6 potassium ion-pair enolates [K–O, 2.631(4),[12a] K–O, 2.664(7) Å[12b]]. The plane through the K,O7,N1 atoms is nearly perpendicular to the mean plane running through the 18-crown-6 oxygens [dihedral angle 87.8(1)°], from which potassium protrudes by 1.058(1) Å. The six oxygen atoms surround the potassium ion in an up and down fashion with respect to the mean plane, as indicated by the out-of-plane distances (Å): O1, 0.428(7); O2, –0.127(7); O3, –0.115(7); O4, 0.140(8); O5A, –0.071(11); O5B, 1.029(18); O6, –0.610(9). The observed geometry is distorted with respect to that found in similar compounds,[13] as a probable consequence of the disorder affecting the crown ether molecules. This disorder could be also taken into account to explain the rather low accuracy of the present analysis. The lengthening of the K–O6 distance [3.254(9) Å] could be similarly accounted for. The chelating behavior of the keto amino enolate anion results in a five-membered chelate ring having an envelope conformation, potassium lying at 2.329(2) Å from the plane through the O7,C27,C28,N1 atoms. This plane is almost parallel to the plane of other oxygens, the dihedral angle being 20.1(2)°. The conformation of the five-membered chelation ring could be best described by the dihedral angle of 72.2(2)° between the planes through the O7,C27,C28,N1 and K,O7,N1 atoms. Bond distances and angles in the keto amino enolate anion are as expected with the double bond mainly localized on the C27–C28 bond [1.360(8) Å]. The phenyl ring is rotated by a torsion angle of 17.5(2)° with respect to the keto amino enolate plane. The maximum displacement from the mean plane through O1,C27,C28,N1 is 0.012(5) Å for C27, indicating the group of atoms O1,C27,C28,N1 to be planar within experimental error.

Although a variety of metal ions have been used for

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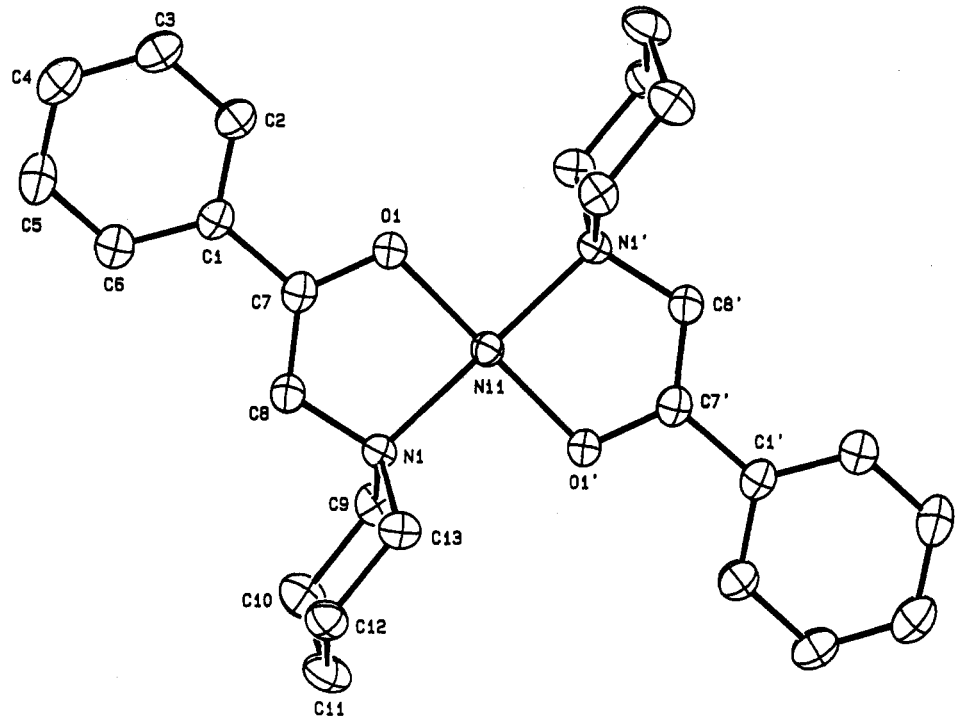
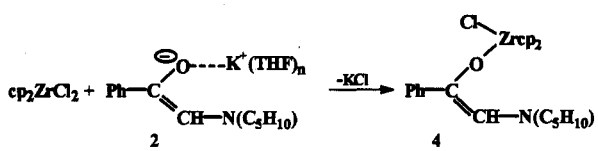


Figure 2. ORTEP drawing of complex **5** (molecule A) (30% probability ellipsoids). Prime denotes a transformation of $-x$, $-y$, $-z$.

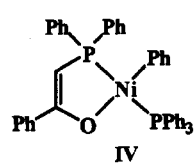
assisting the transformation of β-keto amino enolates, the characterization of metal complexes is practically limited to Zn derivatives[14] containing the enolate in a bidentate form. The reaction of **2** prepared *in situ* followed by the reaction with cp_2ZrCl_2 [cp = η^5-C_5H_5] led to the binding of the enolate to the metal *via* the oxygen atom only.



(2)

This is supported by the presence in the ^{1}H NMR spectrum of an enolic hydrogen at 5.33 ppm and by the absence in the IR spectrum of any C=O band. The properties of the [cp_2ZrCl] fragment binding a single additional atom in the equatorial plane, except in the case of η^2-C,O acyls, rules out any bidentate bonding mode of the amino enolate.[15] The characterization of **4** is reported in the experimental section. The ^{1}H NMR spectrum shows that we are dealing with a single diastereoisomer, *i.e.* the *Z* one (see the discussion of **3**).

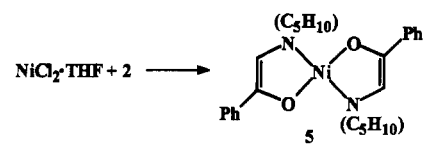
The relevant role played by the nickel(II) complex **IV** and related species containing the β-keto phosphine enolate in the SHOP (shell higher olefin Process) catalytic



IV

process[16] prompted us to explore the complexation of Ni(II) by the β-keto amino enolate **2**. Some preliminary results showed the access to an analogous chemistry, with two major differences being derived from the change in nature of the donor atoms and, by consequence, the nucleophilicity of the carbon enolate. Other nickel and platinum complexes containing N,O bidentate ligands[17] have been found active in some catalytic processes,[18] though such ligands do not have any of the characteristics of an enolato function.

By adding $NiCl_2$ to a THF solution of **2** prepared *in situ*, we isolated **5** as a crystalline solid.



(3)

The diamagnetic complex **5**, a feature which can be attributed to a rather strong field imposed by the β-keto amino enolate anion, has been fully characterized (see Experimental Section), including the single crystal X-ray analysis. Its structure is quite similar to that of the complex having a β-keto phosphino enolate as the ligand, except for the general arrangement of the oxygen atoms, which are *trans* to each other in complex **5**, while they are *cis* in the corresponding phosphorus derivative.[9] Figure 2 shows the molecular structure of **5**, with selected bond distances and angles reported in Table 5. In the asymmetric unit cell there are three half-independent complex molecules, **A**, **B**, and **C**, each one having the nickel atom on a crystallographic center of symmetry. The geometries

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Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 3 and 5

	3	5
formula	$C_{25}H_{30}KNO_7$	$C_{26}H_{32}N_2NiO_2$
a, Å	11.836(2)	9.415(1)
b, Å	16.757(3)	11.533(2)
c, Å	13.899(2)	17.892(3)
α, deg	90	102.81(2)
β, deg	95.55(1)	92.00(2)
γ, deg	90	67.28(2)
V, Å^3	2743.8(8)	1744.6(6)
Z	4	3
fw	495.6	463.3
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
t, °C	22	22
λ, Å	1.541 78	0.710 69
ρ_{calc}, g cm^{-3}	1.200	1.323
μ, cm^{-1}	20.38	8.60
transm coeff	0.644–1.000	0.825–1.000
R	0.081	0.057

[a] $R = \Sigma||\Delta F|/\Sigma|F_o|$.

Table 2. Fractional Atomic Coordinates (×10^4) for Complex 3[a]

atom	x/a	y/b	z/c
K1	1712(1)	−1055(1)	−3387(1)
O1	945(6)	−151(5)	−1922(4)
O2	1591(5)	702(4)	−3393(7)
O3	1930(5)	−81(5)	−5123(6)
O4	1269(6)	−1676(7)	−5244(5)
O5A	33(9)	−2277(6)	−3837(8)
O5B	828(15)	−2670(12)	−3672(12)
O6	−625(7)	−1356(7)	−2385(5)
O7	2576(3)	−1967(2)	−1853(3)
C1	1121(12)	650(9)	−1803(9)
C2	2005(10)	867(6)	−2479(11)
C3	2243(9)	1005(7)	−4087(14)
C4	1731(8)	730(8)	−5044(11)
C5	1442(10)	−418(11)	−5957(8)
C6	1616(12)	−1311(11)	−6042(8)
C7	952(11)	−2478(6)	−5335(8)
C8A	874(14)	−2710(10)	−4283(11)
C8B	383(19)	−2952(13)	−4584(12)
C9	62(13)	−2615(15)	−2919(10)
C10	−803(19)	−2288(16)	−2667(15)
C11	−72(11)	−1317(12)	−1502(11)
C12	133(13)	−441(12)	−1358(9)
N1	4190(4)	−1291(2)	−3052(3)
C21	3116(4)	−1064(3)	−559(4)
C22	3501(5)	−315(4)	−250(4)
C23	3339(6)	−52(4)	687(5)
C24	2780(6)	−509(5)	1295(5)
C25	2389(5)	−1250(5)	997(5)
C26	2538(5)	−1522(4)	63(4)
C27	3233(5)	−1376(3)	−1561(4)
C28	4025(4)	−1040(3)	−2081(4)
C29	4579(5)	−2122(3)	−3089(4)
C30	4586(6)	−2389(4)	−4134(5)
C31	5353(6)	−1855(4)	−4663(5)
C32	5006(6)	−976(4)	−4568(5)
C33	4955(5)	−766(3)	−3510(5)

[a] The site occupation factors are 0.6 for O5A, C8A and 0.4 for O5B, C8B.

of the three molecules are very close. Coordination to nickel is *trans* square planar for symmetry requirements. The five-membered chelate rings are nearly planar in molecules **A** and **B** (maximum out-of-plane distances from the ring plane for C8: 0.012(6) and 0.022(6) Å for molecules **A** and **B**, respectively), while they assume a slightly envelope conformation in **C**, Ni being displaced by 0.056(1) Å from the planar O1,C7,C8,N1 group of atoms. The two β-keto amino enolate ligands are coplanar. Bond distances and angles in the coordination sphere are normal, as well as those within the β-keto amino enolate ligand. As observed in complexes **2** and **3**, the phenyl ring is slightly rotated with respect to the β-keto amino enolate plane, the torsion angle around the C1–C7 bond being 7.9(4), 8.1(5), and 8.0(4)° for molecules **A**, **B**, and **C**, respectively.

The reactivity of complexes derived from β-keto amino enolates is currently being explored.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. NMR spectra were recorded on a 200-AC Bruker instrument.

Preparation of 1. An Et_2O (250 mL) solution of PhCOBr (46.0 g, 250 mmol) was added dropwise to a solution of piperidine (75 mL, 500 mmol) in Et_2O (400 mL) at −20 °C. The solution was vigorously stirred overnight at room temperature, and a white solid formed, which was filtered out and washed with Et_2O (3 × 50 mL). The solvent was evaporated, so obtaining a red oil, which was purified by distillation (95%). IR (THF): ν(C=O) 1684 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.4–1.7 (m, 6 H, CH_2), 2.49 (m, 4 H, CH_2—N), 3.71 (s, 2 H, $COCH_2$—N), 3.52 (s, 2 H, CH_2CO), 7.4–7.6 (m, 3 H, Ph), 8.0 (m, 2 H, Ph).

Preparation of 3. 1 (0.85 g, 4.2 mmol) was added to a THF (50-mL) suspension of KH (0.17 g, 4.2 mmol) and stirred for 2 h. Addition of 18-crown-6 ether (1.11 g, 4.2 mmol) was followed by stirring of the solution for a few minutes. The solvent was evaporated and the yellow oil washed with Et_2O (50 mL). A yellow microcrystalline solid was obtained, which was filtered out and dried (78%). Crystals suitable for X-ray analysis were obtained by extraction with Et_2O. Anal. Calcd for $C_{25}H_{40}KNO_7$: C, 59.38; H, 7.97; N, 2.77. Found: C, 59.62; H, 8.42; N, 2.70. ^{1}H NMR (C_6D_6): δ 1.5–1.8 (m, 6 H, CH_2), 3.18 (s, 28 H, CH_2—N and OCH_2), 5.60 (s, 1 H, =CH), 7.1–7.4 (m, 3 H, Ph), 8.3 (m, 2 H, Ph).

Preparation of 4. To a THF (100-mL) solution of 1 (4.7 g, 23.1 mmol) was added slowly KH (0.932 g, 23.1 mmol). Hydrogen was vigorously evolved. After 4 h a red solution was obtained, which was then cooled to −78 °C. Addition of cp_2ZrCl_2 (6.81 g, 23.3 mmol) was followed by gentle warming of the solution to room temperature with overnight stirring. KCl was filtered off, the solvent evaporated, and Et_2O (50 mL) was added. An orange solid was obtained, which was recrystallized by extraction with Et_2O. Another crop of product was obtained by cooling the flask at −20 °C for 3 days (52%). Anal. Calcd for $C_{23}H_{28}ClNOZr$: C, 60.17; H, 5.71; N, 3.05. Found: C, 60.11; H, 6.03; N, 3.17. IR (Nujol): 1688, 1624, 1591 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.43–1.68 (m, 2 H, CH), 1.69–1.72 (m, 4 H, CH), 2.79 (dd, 4 H, CH_2—N, J = 1.12 Hz). 5.33 (s, 1 H, =CH), 6.38 (s, 10 H, cp), 7.28–7.22 (m, 3 H, Ph), 7.46–7.41 (m, 2 H, Ph).

Preparation of 5. To a THF (100-mL) solution of 1 (3.00 g, 14.8 mmol) was added slowly KH (0.577 g, 14.8 mmol). After 3 h a red solution was obtained, which was cooled to −20 °C. Addition of $NiCl_2$·THF (1.50 g, 7.4 mmol) was followed by gentle warming of the suspension to room temperature with overnight stirring. The resulting red suspension was extracted with the mother liquor, and a microcrystalline orange solid was obtained (48%), which was recrystallized by extraction with Et_2O (30%). Anal. Calcd for $C_{26}H_{32}N_2NiO_2$: C, 67.41; H, 6.96; N, 6.05. Found: C, 68.21; H, 7.22; N, 6.25. IR: 1613, 1546 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.40 (m, 3 H, CH), 1.81 (m, 3 H, CH), 3.16 (ddd, 2 H, CH—N, J = 1.4, 12.43, 12.43 Hz), 3.65 (dd, 2 H, =CH—N, J = 1.4, 12.43 Hz), 5.58 (s, 1 H, =CH), 7.22–7.27 (m, 3 H, Ph), 7.46–7.5 (m, 2 H, Ph).

Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[19] Crystal data and details associated with data collection are given in Tables 1 and SI. Data were collected at room temperature (295 K) on a single crystal diffractometer. For intensities and background

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Table 3. Fractional Atomic Coordinates (×10⁴) for Complex 5

	molecule A			molecule B			molecule C		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Nil	0(–)	0(–)	0(–)	5000(–)	0(–)	0(–)	0(–)	5000(–)	5000(–)
O1	904(4)	–1143(3)	–913(2)	3922(4)	1324(3)	–471(2)	410(5)	6184(4)	4585(2)
N1	–894(4)	1325(4)	–588(2)	5686(4)	–1117(4)	–1014(2)	2051(5)	3783(4)	4615(2)
C1	1232(5)	–1404(5)	–2260(3)	3228(5)	1889(5)	–1683(3)	2263(7)	6569(5)	3911(3)
C2	1868(6)	–2741(5)	–2362(3)	2593(6)	3188(5)	–1326(3)	1384(8)	7882(7)	4095(4)
C3	2451(6)	–3540(5)	–3072(3)	1792(7)	4096(6)	–1741(4)	1814(8)	8720(6)	3761(4)
C4	2439(7)	–3017(6)	–3697(3)	1550(7)	3739(7)	–2491(4)	3071(9)	8218(7)	3257(4)
C5	1845(8)	–1696(7)	–3604(3)	2150(8)	2453(7)	–2858(4)	3929(8)	6909(7)	3086(4)
C6	1258(7)	–902(6)	–2896(3)	2985(7)	1541(6)	–2451(3)	3519(8)	6108(6)	3416(4)
C7	565(5)	–563(5)	–1494(3)	4089(5)	922(4)	–1231(3)	1787(7)	5691(5)	4275(3)
C8	–359(6)	676(5)	–1380(3)	5004(6)	–286(5)	–1546(3)	2746(7)	4480(5)	4264(3)
C9	–312(5)	2392(5)	–308(3)	7418(5)	–1707(5)	–1096(3)	2976(6)	3244(5)	5233(3)
C10	–1112(7)	3556(5)	–664(4)	8044(5)	–2663(5)	–1851(3)	4540(7)	2159(6)	4960(4)
C11	–2838(7)	4072(5)	–527(4)	7456(6)	–3733(5)	–1954(3)	4367(8)	1095(6)	4345(4)
C12	–3412(6)	3005(5)	–839(3)	5713(6)	–3191(5)	–1873(3)	3405(7)	1608(5)	3723(3)
C13	–2613(5)	1871(5)	–476(3)	5097(5)	–2192(5)	–1116(3)	1874(6)	2680(5)	4021(3)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 3

K1–O1	2.761(7)	K1–N1	2.951(5)
K1–O2	2.948(7)	O7–C27	1.300(6)
K1–O3	2.945(9)	N1–C28	1.445(7)
K1–O4	2.785(8)	N1–C29	1.469(6)
K1–O5A	2.880(10)	N1–C33	1.453(7)
K1–O5B	2.915(20)	C21–C27	1.506(8)
K1–O6	3.254(9)	C27–C28	1.360(8)
K1–O7	2.740(4)		
N1–K1–O7	60.8(1)	C28–N1–C33	112.3(4)
K1–O7–C27	89.1(3)	C28–N1–C29	112.3(4)
K1–N1–C33	120.1(3)	O7–C27–C21	116.6(5)
K1–N1–C29	115.6(3)	C21–C27–C28	118.5(5)
K1–N1–C28	83.5(3)	O7–C27–C28	124.9(5)
C29–N1–C33	110.4(4)	N1–C28–C27	122.6(5)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 5

	molecule A	molecule B	molecule C
Nil–O1	1.846(3)	1.840(4)	1.855(5)
Nil–N1	1.951(4)	1.942(3)	1.935(4)
O1–C7	1.323(7)	1.330(6)	1.285(7)
N1–C8	1.453(6)	1.457(7)	1.459(9)
N1–C9	1.515(8)	1.503(6)	1.479(7)
N1–C13	1.495(6)	1.517(8)	1.526(7)
C7–C8	1.328(7)	1.326(6)	1.335(7)
N1–Nil–N1′	180.0(2)	180.0(2)	180.0(2)
N1–Nil–O1′	92.3(2)	91.9(9)	93.0(2)
O1–Nil–N1′	92.3(2)	91.9(2)	93.0(2)
O1–Nil–O1′	180.0(2)	180.0(2)	180.0(2)
O1–Nil–N1	87.6(2)	88.1(2)	87.0(2)
Nil–O1–C7	111.1(3)	111.2(3)	110.9(4)
Nil–N1–C13	109.6(3)	108.9(3)	107.3(4)
Nil–N1–C9	109.1(3)	110.2(3)	111.6(3)
Nil–N1–C8	105.3(3)	105.0(3)	106.4(3)
C9–N1–C13	109.3(4)	108.6(4)	108.4(4)
C8–N1–C13	112.5(4)	111.3(4)	111.2(4)
C8–N1–C9	110.9(4)	112.8(4)	111.8(5)
O1–C7–C1	115.4(5)	116.7(4)	115.9(5)
Nil–C7–C1	156.3(4)	157.3(4)	157.6(4)
Nil–C7–O1	40.9(2)	40.7(2)	41.7(3)
C1–C7–C8	124.1(5)	123.6(5)	121.5(6)
O1–C7–C8	120.4(5)	119.7(5)	122.5(6)
Nil–C7–C8	79.6(3)	79.1(3)	80.8(4)
N1–C8–C7	115.5(5)	115.9(5)	113.1(6)

[a] Primes refer to transformations of $-x, -y, -z$, $1-x, -y, -z$, and $-x, 1-y, 1-z$ for molecules A, B, and C, respectively.

individual reflection profiles were analyzed.[20] The structure amplitudes were obtained after the usual Lorentz and polarization corrections[21] and the absolute scale was established by the Wilson method.[22] Data were corrected for absorption using the program ABSORB.[23] The function minimized during the full matrix least-squares refinement was $\Delta w|\Delta F|^2$. Unit weights were used since these gave a more satisfactory analysis of variance and the best agreement factors.[21] Anomalous scattering corrections were included in all structure factor calculations.[24b] Scattering factors for neutral atoms were taken from ref 24a for non-hydrogen atoms and from ref 25 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom Patterson map for **5**. For **3** the structure was solved using SHELX86.[26] Refinement was first done isotropically and then anisotropically for non-H atoms, excepting those affected by disorder. The structures of both complexes were refined straightforwardly. For **3** an oxygen atom (O5) and a methylene carbon (C8) were found to be disordered over two positions (**A** and **B**) and were isotropically refined with the site occupation factors given in Table 2. During the refinement of complex **3** a constraint was imposed to the bond distances involving the disordered atoms.

For both complexes the hydrogen atoms were located from difference Fourier maps. They were introduced in the subsequent refinements as fixed atom contributions with isotropic U values fixed at 0.15 and 0.08 Å², for **3** and **5**, respectively. Hydrogen atoms related to the disordered carbon atoms in complex **3** were ignored.

The final difference map showed no unusual features, with no significant peak above the general background. Final atomic coordinates are listed in Tables 2 and 3 for non-H atoms and in Tables SII and SIII for hydrogens. Thermal parameters are given in Tables SIV and SV; selected bond distances and angles, in Tables SVI and SVII.[27]

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (Tables SI–SVII) for complexes **3** and **5** (10 pages). Ordering information is given on any current masthead page.

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