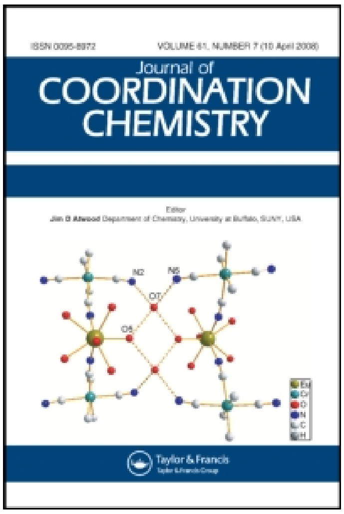

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Cis-Trans Isomerism in Mononuclear Nickel(II) β-Ketoenamine Complexes

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To cite this Article Maverick, Andrew W. , Fronczek, Frank R. , Martone, Daniel P. and Bradbury, Julie R.(1989) 'Cis-Trans Isomerism in Mononuclear Nickel(II) β-Ketoenamine Complexes', Journal of Coordination Chemistry, 20: 2, 149 — 161
To link to this Article: DOI: 10.1080/00958978909408861
URL: http://dx.doi.org/10.1080/00958978909408861

J. Coord. Chem. 1989, Vol. 20, pp. 149-161
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CIS-TRANS ISOMERISM IN MONONUCLEAR NICKEL(II) β-KETOENAMINE COMPLEXES

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(Received January 3, 1989)

Solution NMR and X-ray crystallographic structural studies of square-planar nickel(II) Schiff base complexes are reported. In contrast to recently prepared cofacial binuclear complexes derived from bis(β-ketoenamines), which have the *cis* arrangement of O and NH donors about each metal atom, two representative mononuclear complexes, Ni(acim)$_2$ (acimH = 4-amino-3-penten-2-one) and Ni(bzacim)$_2$ (bzacimH = 3-amino-1-phenyl-2-buten-1-one), are produced as *trans* isomers. Ni(acim)$_2$ ($NiC_{10}H_{16}N_2O_2$) is orthorhombic, space group *Ccca*, $a = 16.770(2)$, $b = 15.054(2)$, $c = 13.494(1)$ Å, $Z = 12$, $R = 0.055$, $R_w = 0.042$ for 143 parameters and 1748 reflections with $I > 1\sigma(I)$. Ni(bzacim)$_2$ ($NiC_{20}H_{20}N_2O_2$) is monoclinic, space group $P2_1/c$, $a = 5.9186(8)$, $b = 13.694(2)$, $c = 11.944(4)$ Å, $\beta = 112.18(2)°$, $Z = 2$, $R = 0.038$, $R_w = 0.037$ for 156 parameters and 1589 reflections with $I > 2\sigma(I)$. Crystals of Ni(bzacim)$_2$ contain centrosymmetric, nearly planar *trans* molecules. The structure of Ni(acim)$_2$ contains independent molecules with 2 and 222 symmetry, but both of these are disordered, so that whether the *cis* or *trans* isomer is present cannot be determined. However, solution ^{1}H NOE and lanthanide shift measurements indicate that the *trans* isomer predominates for both compounds.

Keywords: Nickel(II), Schiff base, stereochemistry, crystal structure, NMR

INTRODUCTION

Square-planar complexes of Schiff base ligands constitute one of the most widely investigated classes of transition-metal complexes. A large number of these species have been prepared from β-ketoenamine ligands, as shown in Scheme I. In Ni(acen) (1),[†] ethylenediamine is used to join the two β-diketone moieties, and the arrangement of O and N atoms about the metal atom is constrained to be *cis*. Bidentate ligands derived from amines RNH_2 (R = alkyl or aryl) lead exclusively to *trans*

[†] Ligand abbreviations: acacH = 2,4-pentanedione; acimH = acetylacetone imine (4-amino-3-penten-2-one); bzacimH = benzoylacetone imine (3-amino-1-phenyl-2-buten-1-one); admhH = pivaloylacetone imine (5-amino-2,2-dimethyl-4-hexen-3-one); acenH$_2$ = bis(acetylacetone)ethylenediimine (4,4'-[1,2-ethanediyldinitrilo]-bis(2-pentanone)); bzacenH$_2$ = bis(benzoylacetone)ethylenediimine (3,3'-[1,2-ethanediyldinitrilo]-bis(1-phenyl-1-butanone)); salenH$_2$ = bis(salicylaldehyde)ethylenediimine (2,2'-[1,2-ethanediylbis(nitrilomethylidyne)]bis(phenol)); fodH = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione; BBIH$_2$ = [5-(1,1-dimethylethyl)-1,3-phenylenebis(methylene)]bis(4-amino-3-penten-2-one).

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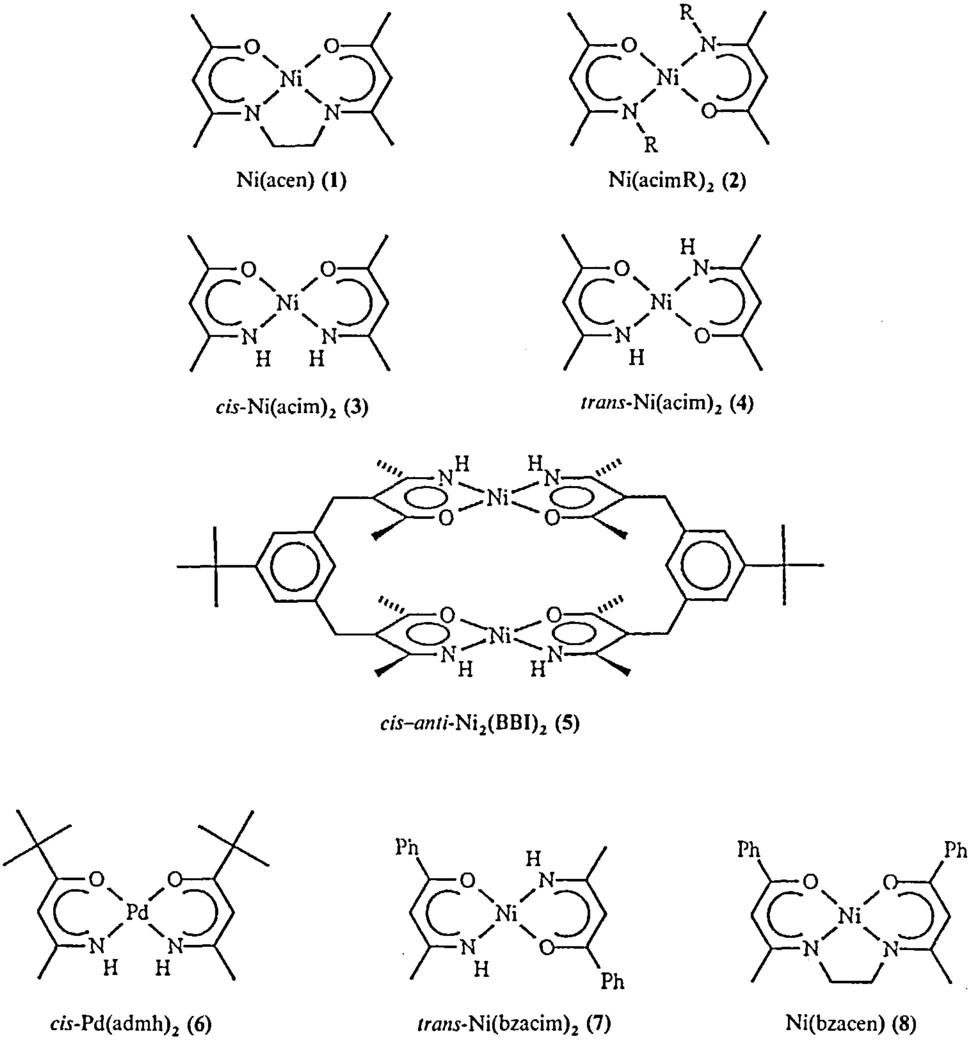
isomers **2** for steric reasons. (For bulky R groups, distortion of **2** to produce pseudotetrahedral, paramagnetic complexes is often facile.[1]) Unsubstituted β-ketoenamines prepared from NH_3, however, can in principle produce either *cis* (**3**) or *trans* (**4**) isomers.



Ni(acen) (**1**)

Ni(acimR)$_2$ (**2**)

cis-Ni(acim)$_2$ (**3**)

trans-Ni(acim)$_2$ (**4**)

cis-anti-Ni$_2$(BBI)$_2$ (**5**)

cis-Pd(admh)$_2$ (**6**)

trans-Ni(bzacim)$_2$ (**7**)

Ni(bzacen) (**8**)

SCHEME 1 Mononuclear and binuclear nickel(II) Schiff base complexes.

We have recently begun studying binuclear analogues of these complexes as potential catalysts for multielectron redox reactions. X-ray analysis shows that the bis(β-ketoenamine) complexes $Ni_2(BBI)_2$ (**5**) and $Pd_2(BBI)_2$ have the *cis-anti* geometry.[2] We were therefore interested in whether the corresponding mononuclear complexes are *cis* or *trans*. Surprisingly, although the complexes have generally been assumed to be *trans* (**4**), there is very little direct evidence in the literature for either isomer. Many of the assumptions are based on a preliminary study of the crystal structure of Ni(acim)$_2$, in which the space group and unit-cell dimensions were determined.[3] More recently the *cis* (6) and *trans* isomers of the palladium(II) β-ketoenamine complex Pd(admh)$_2$ have been prepared and separated, and their interconversion studied.[4] Herein we report a fuller investigation of Ni(acim)$_2$, whose disordered structure is actually compatible with either isomer, the crystal structure of *trans*-Ni(bzacim)$_2$ (7), and ^{1}H NMR evidence that the *trans* isomers predominate in solution for both complexes.

EXPERIMENTAL

Materials and Procedures

The method of Lacey[5] was used to prepare Ni(acim)$_2$. The following method was used to prepare bzacimH: an approximately 0.12 M solution of benzoylacetone (Aldrich) in conc. NH_3 (aq), prepared by slight warming, was warmed further until it became turbid. The mixture was then cooled to −15°C and the resulting solid collected and washed with a small amount of CH_3OH at the same temperature. The compound was crystallized from a saturated solution in CH_3OH by adding three times its volume of conc. NH_3(aq) and cooling to −15°C; m.p. 141–143°C (lit.[6] 143°C). Solutions of Ni(OAc)$_2$·4H_2O(MCB; 0.44 g, 1.8 mmol) in 10% NH_3(aq) and bzacimH (0.57 g, 3.5 mmol) in ethanol (25 cm^3 each) were warmed together, producing a red-brown crystalline precipitate of Ni(bzacim)$_2$. Identical material was obtained by mixing solutions of $Ni(NO_3)_2 \cdot 6H_2O$, triethylamine, and bzacimH (mol ratio 1:2:2) in DMF. ^{13}C NMR in $CDCl_3$: δ 24.4 (CH_3CO), 25.3 (CH_3CNH), 97.2 (CH), 166.7 (CNH), 176.3 (CO) ppm *vs* TMS.

Crystals of the nickel complexes suitable for X-ray diffraction were obtained by cooling of a hot saturated solution in acetone (Ni(acim)$_2$) or from dichloromethane by layering with hexane (Ni(bzacim)$_2$). NMR spectra were measured using Bruker AC100 or AC200 instruments; chemical shift values were reproducible within *ca* ±0.003 ppm. Lanthanide shift experiments employed solutions *ca* 0.03 M in Ni(acim)$_2$ or Ni(bzacim)$_2$. Electronic absorption spectra were recorded by using Cary 14 or Cary 219 spectrophotometers.

Crystallography

An Enraf-Nonius CAD4 diffractometer, fitted with a MoK$_\alpha$ source (λ = 0.71073 Å) and graphite monochromator, was used to measure the diffracted intensities. The space groups were uniquely determined by systematic absences in the diffraction data. The structures were solved by using the Enraf-Nonius SDP set of programs. Initial coordinates for all non-hydrogen atoms were obtained by direct methods. Except as noted below, all hydrogen atoms were located in difference Fourier maps, and their coordinates and isotropic displacement parameters were refined. Data for the two structures were corrected for absorption (ψ scans). Additional data are summarized in Table I.

TABLE I

Data collection and refinement parameters.[a]

	$Ni(acim)_2$	$Ni(bzacim)_2$
Formula (fw)	$NiC_{10}H_{16}N_2O_2$ (254.94)	$NiC_{20}H_{20}N_2O_2$ (379.08)
Colour, habit	red, parallelepiped	red-orange, parallelepiped
Cryst. dimen./mm	0.13 × 0.20 × 0.50	0.20 × 0.23 × 0.28
Space group	*Ccca* (No. 68)	$P2_1/c$ (No. 14)
a/Å	16.770(2)	5.9186(8)
b/Å	15.054(2)	13.694(2)
c/Å	13.494(1)	11.944(4)
β/°	–	112.18(2)
V/Å^3	3407(1)	896.3(7)
Z	12	2
ρ_x/g cm^{-3}	1.491	1.405
ρ_m/g cm^{-3}	1.48(2)	1.38(2)
T/°C	24	26
μ(MoK$_\alpha$)/cm^{-1}	16.97	11.00
Abs. corr., transm. range	0.9009–0.9976	0.9531–0.9999
θ range/°	1–35	1–30
Octants collcd.	$h\,k\,l$	$h\,k\,\pm l$
Reflns. measd.	3752	2614
Reflns. obsd. (threshold)	1748 ($I > 1\sigma(I)$)	1589 ($I > 2\sigma(I)$)
R_{INT}[b]	–	0.016
Parameters	143	156
R[c]	0.055	0.038
R_w[d]	0.042	0.037
P[e]	0.02	0.02
GOF[f]	1.763	1.668
Max. shift/esd	0.01	0.05
Max. (min.) diff. pk/e Å^{-3}	0.67 (−0.43)	0.52 (−0.26)

[a] In Tables I–IV, estimated standard deviations in the least significant digits of the values are given in parentheses. [b] Agreement factor on I for equivalent observed reflections. [c] $R = \Sigma||F_o|-F_c||/|F_o|$. [d] $R_w = \sqrt{[\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]}$. [e] Instability factor in non-Poisson weighting scheme: $w = 4F_o^2[\sigma^2(I) + (P\cdot F_o^2)^2]^{-1}$. [f] $\mathrm{GOF} = \sqrt{[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]}$.

Ni(acim)$_2$

After the initial refinement of non-hydrogen atom coordinates and isotropic displacement parameters, a difference Fourier map revealed electron density peaks corresponding to imino H atoms near all atoms bound to Ni. Therefore, all of these atoms were modelled as superposed O and N atoms, each with occupancy 0.5, and with coordinates and displacement parameters constrained to be equal; all imino H atoms were also given 0.5 occupancy. Coordinates for the imino H atoms and one of the methyl H atoms (H43A) failed to refine satisfactorily; these atoms were thus fixed at positions indicated by the difference Fourier maps.

Ni(bzacim)$_2$

Crystals of this complex were reported to be isomorphous with those of $Cu(bzacim)_2$.[7] However, the non-hydrogen atom coordinates from the copper structure did not serve as a successful starting point for least-squares refinement of the Ni(bzacim)$_2$ structure. Unit-cell parameters (Table I) and final coordinates (Table II) for Ni(bzacim)$_2$ are substantially different from those of Cu(bzacim)$_2$.

TABLE II

Fractional coordinates and isotropic equivalent displacement parameters for non-hydrogen atoms.[a]

Atom	x/a	y/b	z/c	B_{eqv}(Å^2)
		A. Ni(acim)$_2$		
Ni1A	0.16663(3)	$\frac{1}{4}$	$\frac{1}{4}$	2.326(7)
Ni1B	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	2.51(1)
NO1A[b]	0.0860(1)	0.2969(1)	0.1717(2)	3.06(5)
NO1B[b]	0.4196(1)	0.3342(1)	0.2592(2)	3.07(4)
NO2A[b]	0.2472(1)	0.2933(1)	0.1697(2)	3.08(4)
C1A	0.0943(2)	0.3428(2)	0.0904(2)	2.92(6)
C1B	0.4279(2)	0.4200(2)	0.2622(2)	2.80(5)
C2A	0.1666(2)	0.3640(2)	0.0492(2)	3.60(6)
C2B	$\frac{1}{2}$	0.4626(2)	$\frac{1}{4}$	3.28(8)
C3A	0.2395(2)	0.3389(2)	0.0882(2)	3.10(6)
C3B	0.3537(2)	0.4739(2)	0.2773(3)	4.16(7)
C4A	0.0184(2)	0.3723(2)	0.0410(3)	4.81(8)
C5A	0.3154(2)	0.3643(2)	0.0361(3)	4.68(8)
		B. Ni(bzacim)$_2$		
Ni	0	0	0	3.730(8)
O1	0.2158(2)	−0.0633(1)	0.1335(1)	4.15(3)
N2	−0.1673(3)	0.0575(1)	0.0851(2)	4.20(4)
C3	0.2279(3)	−0.0561(2)	0.2446(2)	3.66(5)
C4	0.0763(4)	0.0001(2)	0.2799(2)	4.11(5)
C5	−0.1210(4)	0.0548(2)	0.2010(2)	3.82(5)
C6	0.4241(4)	−0.1171(2)	0.3320(2)	3.79(5)
C7	0.4270(4)	−0.1411(2)	0.4464(2)	5.13(6)
C8	0.6053(5)	−0.2003(2)	0.5218(2)	6.49(8)
C9	0.7839(5)	−0.2380(2)	0.4888(3)	6.28(8)
C10	0.7870(4)	−0.2143(2)	0.3778(2)	5.68(7)
C11	0.6089(4)	−0.1544(2)	0.3002(2)	4.50(6)
C12	−0.2787(4)	0.1104(2)	0.2512(2)	5.05(6)

[a] B_{eqv} is the equivalent isotropic displacement parameter $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac \cos \beta \, \beta_{13}]$. [b] O and N atoms (occupancy 0.5 each), with positional and displacement parameters constrained to be equal.

RESULTS AND DISCUSSION

Description of Structures

Ni(acim)$_2$

Two independent molecules are present in this structure, one with crystallographically imposed 2 (C_2) symmetry (eight molecules per unit cell; atoms labelled "A" in the ORTEP[8] drawing of Figure 1) and one with 222 (D_2) symmetry (four molecules per unit cell; "B"). The molecules at the 222 ("B") sites must be disordered, since the maximum symmetry of Ni(acim)$_2$ is *mm*2 (C_{2v}, *cis*) or 2/*m* (C_{2h}, *trans*). Although it was claimed in the previous study of Ni(acim)$_2$[5] that the molecules at the lower-symmetry "A" site must be *trans*, the orientation of the two-fold axis at this site (see drawing) is actually consistent with an ordered structure only if it is *cis*. In fact, however, the "A" molecules are disordered as well; peaks corresponding to the half-populated hydrogen atoms appeared in the difference Fourier maps near both NO1A and NO2A, and the refined displacement parameters for the $\frac{1}{2}$(N + O) atoms are reasonable. Therefore, the arrangement of the molecules in the crystal is too highly disordered for the direct determination of which isomer is present.

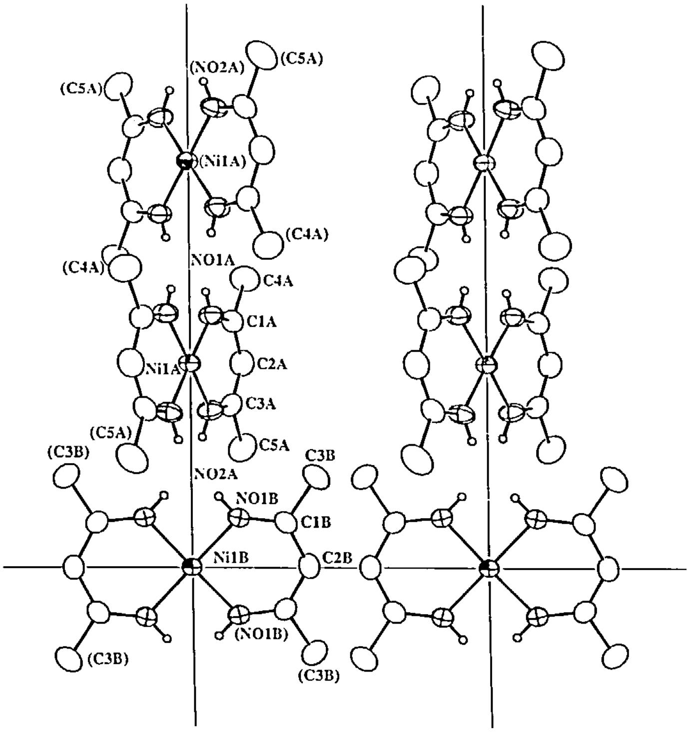


FIGURE 1 ORTEP[8] stereoscopic drawing for Ni(acim)$_2$, with *a* vertical and *b* horizontal. The total vertical length shown is approximately half of the *a* dimension (*ca* 8.5 Å). Thermal ellipsoids are drawn at the 50% probability level, and all H atoms except those in the disordered imino groups are omitted for clarity. The crystallographically independent molecules "A" (site symmetry 2) and "B" (site symmetry 222) are shown, along with the two-fold axes parallel to *a* and *b*. A total of four asymmetric units are shown (two "A" molecules and one "B" molecule) in order to illustrate intermolecular contacts (see text).

The packing arrangement in the crystal provides no new information concerning the isomer distribution; no unusual intermolecular contacts (which might be suggestive of a preference for one isomer) are observed. The closest such contacts are along the twofold axis parallel to *a* (see Figure 1), both between adjacent "A" molecules (NO1A–NO1A, 3.21 Å) and between "A" and "B" molecules (NO1B–NO2A, 3.19 Å). Both of these are consistent with weak NH–O hydrogen bonding, and therefore a molecule at one site will probably pack most efficiently with the same isomer at adjacent sites. However, neither *cis* nor *trans* can be ruled out on this basis.

One of the CH_3 hydrogen atoms in Ni(acim)$_2$ approximately eclipses each of the imino H atoms in the chelate rings. We have observed similar conformations in the structures of bis(β-diketone)[9,10] and bis(β-ketoenamine)[2] complexes.

TABLE III
Bond distances (Å).

Atoms	Distance	Atoms	Distance	Atoms	Distance
		A. Ni(acim)$_2$			
Ni1A-NO1A	1.856(2)	C1A-C2A	1.371(4)	Ni1B-NO1B	1.854(2)
Ni1A-NO2A	1.850(2)	C1A-C4A	1.505(4)	NO1B-C1B	1.300(3)
NO1A-C1A	1.304(4)	C2A-C3A	1.383(5)	C1B-C2B	1.380(3)
NO2A-C3A	1.302(3)	C3A-C5A	1.504(5)	C1B-C3B	1.498(4)
		B. Ni(bzacim)$_2$			
Ni-O1	1.841(1)	C3-C6	1.490(2)	C7-C8	1.366(3)
Ni-N2	1.842(2)	C4-C5	1.408(3)	C8-C9	1.362(4)
O1-C3	1.304(2)	C5-C12	1.494(3)	C9-C10	1.371(3)
N2-C5	1.306(2)	C6-C7	1.400(3)	C10-C11	1.380(3)
C3-C4	1.364(3)	C6-C11	1.383(3)		

TABLE IV
Bond angles (°).

Atoms	Angle	Atoms	Angle	Atoms	Angle
		A. Ni(acim)$_2$			
NO1A-Ni1A-NO1A	86.4(1)	NO1A-C1A-C4A	116.0(3)	NO1B-Ni1B-NO1B	93.80(8)
NO1A-Ni1A-NO2A	93.70(9)	C2A-C1A-C4A	119.9(3)	NO1B-Ni1B-NO1B	172.3(1)
NO1A-Ni1A-NO2A	178.13(9)	C1A-C2A-C3A	124.2(3)	Ni1B-NO1B-C1B	127.2(2)
NO2A-Ni1A-NO2A	86.2(1)	NO2A-C3A-C2A	123.6(3)	NO1B-C1B-C2B	123.5(3)
Ni1A-NO1A-C1A	127.0(2)	NO2A-C3A-C5A	116.4(3)	NO1B-C1B-C3B	117.0(2)
Ni1A-NO1A-C3A	127.4(2)	C2A-C3A-C5A	120.0(3)	C2B-C1B-C3B	119.5(2)
NO1A-C1A-C2A	124.0(3)	NO1B-Ni1B-NO1B	86.72(8)	C1B-C2B-C1B	124.5(3)
		B. Ni(bzacim)$_2$			
O1-Ni-N2	93.72(6)	C3-C4-C5	124.7(2)	C7-C6-C11	117.5(2)
Ni-O1-C3	126.8(1)	N2-C5-C4	120.9(2)	C6-C7-C8	120.3(2)
Ni-N2-C5	129.1(1)	N2-C5-C12	119.8(2)	C7-C8-C9	121.6(2)
O1-C3-C4	124.5(2)	C4-C5-C12	119.2(2)	C8-C9-C10	119.1(2)
O1-C3-C6	113.5(2)	C3-C6-C7	122.3(2)	C9-C10-C11	120.2(2)
C4-C3-C6	121.9(2)	C3-C6-C11	120.2(2)	C6-C11-C10	121.2(2)

Ni(bzacim)$_2$

The structure consists of centrosymmetric molecules, with a nearly planar *trans* arrangement about the Ni atoms. An ORTEP drawing of the molecule is shown in Figure 2. The phenyl ring (C6–C11) makes an angle of 17.3(2)° with the β-ketoiminato chelate ring (O1, C3, C4, C5, N2), which is planar within 0.006 Å. The nickel atom is displaced 0.082 Å out of the chelate ring. This displacement, combined with the inversion symmetry of the molecule, results in a slightly "stepped" structure. The perpendicular distance between the two chelate rings (*s*, according to the description of these stepped structures by Holm and co-workers[11]) is 0.16 Å. The crystal contains parallel stacks of molecules arranged along the *a* axis. The major difference between the present structure and that of Cu(bzacim)$_2$[7] is that the individual molecules are more closely parallel to the *bc* plane in Ni(bzacim)$_2$.

In contrast with Ni(acim)$_2$ and with our previously determined binuclear structures, the hydrogen atoms at C12 in Ni(bzacim)$_2$ do not eclipse either H4 or H2N (for example, the torsion angle C4–C5–C12–H121 is −155°). No significant intermolecular contacts are observed.

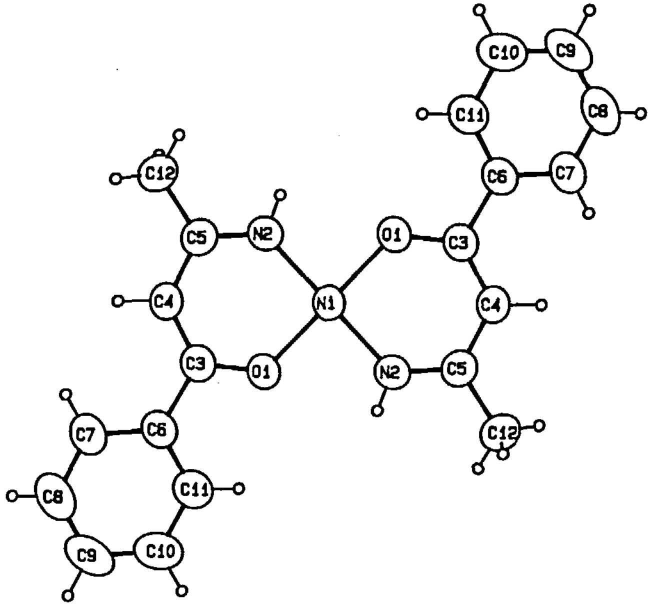


FIGURE 2 ORTEP[8] drawing for Ni(bzacim)$_2$, with thermal ellipsoids drawn at the 50% probability level.

Cis–trans *Isomerism in Solution*

Electronic spectra

As mentioned above, planar bis(β-ketoiminato)nickel(II) complexes can form two isomers only when the imino N atoms are unsubstituted (*i.e.* NH). By comparing its electronic absorption spectrum with those of other complexes of known stereochemistry, Archer concluded that Ni(acim)$_2$ possesses the *trans* geometry.[12] He observed two low-energy absorption maxima for Ni(acim)$_2$ and for other complexes with *trans*-N_2O_2 environments about Ni, but only one band for Ni(acen) and Ni(salen), both of which are constrained to be *cis*.

We have measured the electronic spectrum of Ni(acim)$_2$ as well as those of Ni(acen) and Ni$_2$(BBI)$_2$ (see Table V). We find small shoulders at higher energy in all three spectra. These data suggest that the absorption spectrum in the 400–500 nm region may not be sufficient to distinguish between *cis* and *trans* isomers.

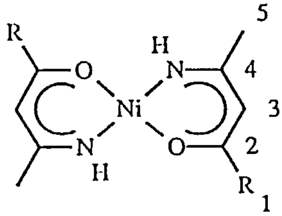
TABLE V
Electronic spectral data for nickel(II) Schiff base complexes.[a]

Complex	λ_{max}/nm (ε/M^{-1} cm^{-1})
Ni(acen)	565 (80);[b] 458 (30)[c]
Ni(acim)$_2$	552 (43); 435 (85)[b]
Ni$_2$(BBI)$_2$	555 (150); 458 (40)[c]

[a] Measured in CHCl$_3$ solution. The higher-energy bands are shoulders, and therefore the values of λ_{max} and ε are probably uncertain by ±10 nm and ±50% respectively. [b] Ref 12. [c] This work.

TABLE VI
^{1}H NMR chemical shifts.[a]

Complex	Solvent	C-1	C-3	C-5	NH	aromatic
Ni(acim)$_2$	CDCl$_3$	1.72	4.82	1.87	5.0	
Ni(acim)$_2$	C$_6$D$_6$	1.73	4.72	1.24	5.0	
Ni(acim)$_2$	CD$_2$Cl$_2$	1.68	4.84	1.86	ca. 5.0	
Ni(bzacim)$_2$	CDCl$_3$		5.53	2.05	5.4	7.3m, 7.6m



Ni(acim)$_2$ (R = CH$_3$)
Ni(bzacim)$_2$ (R = Ph)

[a] δ/ppm *vs* TMS, 20–25°C.

NMR measurements

Since neither the crystal structure nor the electronic absorption spectrum of Ni(acim)$_2$ reveals unambiguously which isomer is present, we examined the ^{1}H NMR spectra of solutions of Ni(acim)$_2$ and Ni(bzacim)$_2$ in the presence of the lanthanide shift reagent Eu(fod)$_3$. Experiments of this type with Schiff base complexes were first reported by Lindoy and Moody.[13] They observed a downfield shift of *ca* 9.3 ppm in the resonance for the methyl group adjacent to the carbonyl O atom of Ni(acen) (**1**) when it was treated with a slight excess of Eu(fod)$_3$. They attributed this shift to chelation of the *cis* O atoms in Ni(acen) to the paramagnetic Eu atom.

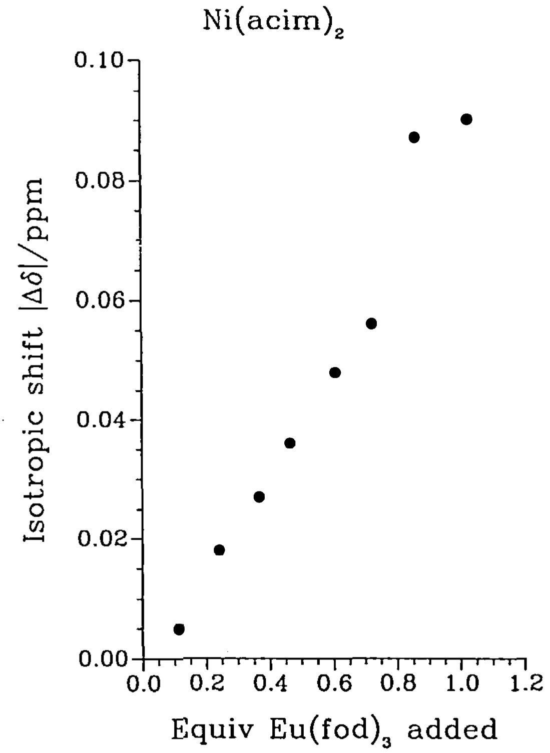


FIGURE 3 Isotropic shifts in the CH_3CO ^1H resonance of Ni(acim)$_2$ on addition of Eu(fod)$_3$ ($CDCl_3$, room temperature).

We observe shifts in the Ni(acim)$_2$ spectrum on addition of Eu(fod)$_3$ (see Figure 3), but the effects are much smaller; 1 equiv of Eu(fod)$_3$ causes a shift of only 0.090 ppm. Assuming that the affinity of *cis*-Ni(acim)$_2$ for Eu(fod)$_3$ is similar to that of Ni(acen), no more than *ca* 1% of Ni(acim)$_2$ can be in the *cis* form.[††]

We wished to compare the above data, which strongly favour the *trans* isomer for Ni(acim)$_2$ in solution, with Ni(bzacim)$_2$, which is *trans* in the solid state. In this case the most closely related *cis* complex is Ni(bzacen), 8. Lindoy and Moody observed a shift of 0.23 ppm in the methine resonance for Ni(bzacen) on treatment with Eu(fod)$_3$. The shift is probably smaller than those for Ni(acen) because of steric interference from the phenyl groups in Ni(bzacen). We observe a shift of less than 0.01 ppm in the Ni(bzacim)$_2$ methine resonance on addition of Eu(fod)$_3$. This indicates that Ni(bzacim)$_2$ is also predominantly *trans* in solution.

The results described above for solutions of Ni(acim)$_2$ and Ni(bzacim)$_2$ favour the *trans* isomer in crystalline Ni(acim)$_2$ as well.

[††] The 1% figure should be regarded as an upper limit, for two reasons. First, the *trans* form may also show an isotropic shift on treatment with Eu(fod)$_3$. Second, selective binding of Eu(Fod)$_3$ to *cis*-Ni(acm)$_2$ will favour formation of the *cis* isomer (see reactions 1 and 2).

NMR chemical-shift assignments

The largest shift in the ^1H spectrum of $Ni(acim)_2$ on treatment with $Eu(fod)_3$ occurs for the methyl resonance at 1.72 ppm, indicating that this resonance is attributable to CH_3CO and therefore that the CH_3CNH resonance lies at 1.87 ppm. This was surprising, since O ordinarily exerts a greater electron-withdrawing effect than N; as a result, CH_3CO resonances are often found farther downfield than the CH_3CNH resonance. We wished to use ^1H NOE measurements to confirm this new assignment; irradiation of the NH resonances should cause an increase in the intensity of the CH_3CNH resonance (minimum H–H distance *ca* 2.0 Å; in the *trans* isomer, the closest distance between NH and CH_3CO is *ca* 3.7 Å.)

We were unable to make the NOE measurement in $CDCl_3$, since the NH and CH (methine) resonances overlap. However, both the NOE and the $Eu(fod)_3$ experiments can be performed in C_6D_6, in which the NH and CH chemical shifts differ by *ca* 0.5 ppm. Treatment of $Ni(acim)_2$ with $Eu(fod)_3$ in C_6D_6 causes the largest shift in the 1.74 ppm resonance. Also, irradiation at 5.2 ppm (NH) leads to a positive NOE in the 1.25 ppm resonance. Therefore, the 1.25 and 1.74 ppm resonances are due to CH_3CNH and CH_3CO, respectively (Dilli and Maitra observed that chemical shifts for $Ni(acim)_2$ and related complexes are solvent-sensitive;[14] however, they did not distinguish the CH_3CNH and CH_3CO resonances).

A separate ^1H-^{13}C shift-correlation measurement (see spectrum in supplementary material) shows that the ^1H resonances at 1.72 (CH_3CO) and 1.87 ppm (CH_3CNH) in $CDCl_3$ are correlated with the ^{13}C resonances at 24.4 and 25.3 ppm respectively; therefore, the methyl resonances in the ^{13}C spectrum (see Experimental Section) can also be assigned for the first time.

Energetics of cis–trans *isomerization in Ni(acim)$_2$*

ΔG^0_{tc} for isomerization of $Ni(acim)_2$ (*1*) may be estimated from the $Eu(fod)_3$ experiments, if the affinity of $Eu(fod)_3$ for *cis*-$Ni(acim)_2$ (*2*) is also included.

$$trans\text{-Ni(acim)}_2 \rightleftharpoons cis\text{-Ni(acim)}_2 \quad K_{tc} \qquad (1)$$

$$cis\text{-Ni(acim)}_2 + \text{Eu(fod)}_3 \rightleftharpoons cis\text{-Ni(acim)}_2\cdot\text{Eu(fod)}_3 \quad K_{Eu} \qquad (2)$$

Our lanthanide-shift data (*e.g.*, *ca* 1% *cis* isomer present when total Ni and Eu concentrations are 0.03 M) yield a value of *ca* $0.3\ M^{-1}$ for $K_{tc}K_{Eu}$ in $CDCl_3$. Assuming that K_{Eu} is similar to the value Lindoy and Moody[13] found for Ni(acen) ($>1000\ M^{-1}$), K_{tc} may be no larger than 3×10^{-4}, corresponding to $\Delta G^0_{tc} = 20\ kJ\ mol^{-1}$.

The substantial stability of *trans*-$Ni(acim)_2$ may be due in part to steric repulsion between the nonbonded imino H atoms in the *cis* form. However, this repulsion is unlikely to account for all of the observed isomerization energy; a molecular-mechanics calculation using the SYBYL program[15] suggests that the *trans* isomer is more stable by only *ca* $2\ kJ\ mol^{-1}$. The remainder of the free-energy difference may therefore represent a significant electronic preference for the *trans* isomer. Such a preference would be different from the $Pd(admh)_2$ system, in which K_{tc} is close to 1,[4] and from planar O_2S_2 complexes, in which the *cis* isomer is favoured.[16]

Holm and co-workers have studied extensively the planar and pseudotetrahedral forms of nickel(II) Schiff base complexes. It is likely that the *cis–trans* isomerization of $Ni(acim)_2$ occurs *via* such a pseudotetrahedral intermediate (another possible route, ligand dissociation, is much slower than the planar-tetrahedral equilibrium[17]). However, Everett and Holm observed no paramagnetic shifts attributable to the pseudotetrahedral form of $Ni(acim)_2$ even at 85°C.[18] Assuming that a contact shift of 5 Hz would have been detectable by Everett and Holm, a lower limit for the *cis–trans* isomerization barrier is *ca* 20 kJ mol^{-1}. In order to estimate the barrier further, we studied the ^1H NMR spectrum of $Ni(acim)_2$ at low temperature. If isomerization is slow on the NMR time scale, four methyl resonances are expected, and if $Ni(acim)_2$ is similar to $Pd(admh)_2$,[4] the *cis* and *trans* methyl resonances may differ by *ca* 0.04 ppm. We observe essentially no change in the spectrum of $Ni(acim)_2$ in CD_2Cl_2 even at −85 °C. This suggests that the barrier is no larger than 40 kJ mol^{-1}.[19]

Cis–trans *Isomerism in Binuclear Complexes*

We began the present work largely because of the unusual *cis* geometry adopted by $Ni_2(BBI)_2$ and $Pd_2(BBI)_2$.[2] The lanthanide-shift technique discussed here is likely to be useful for identifying isomers in new binuclear systems.

The *trans* isomer appears to be favoured in the mononuclear complexes. The preferential formation of *cis–anti*-$Ni_2(BBI)_2$ in DMF is due to weak hydrogen bonding with the solvent. Some additional stabilization may also result from the high polarity of DMF, which is expected to favour the *cis* isomer. We attempted to prepare *cis*-$Ni(bzacim)_2$ by a similar procedure (by mixing $Ni(NO_3)_2{\cdot}6H_2O$, bzacimH and Et_3N in DMF), but only the *trans* isomer (shown crystallographically) formed. This suggests that, even if *cis* complexes can be prepared initially, they will be stable only if isomerization is sterically impossible.

ACKNOWLEDGMENTS

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

SUPPLEMENTARY MATERIAL

^1H-^{13}C shift-correlation spectrum of $Ni(acim)_2$ (1 page), tables of hydrogen-atom parameters, bond distances and angles involving hydrogen atoms, anisotropic displacement parameters (5 pages) and tables of observed and calculated structure factors (21 pages) are available from the Authors.

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19. Substantial line broadening would be expected at −85°C for resonances differing by 0.05 ppm (10 Hz in a 200-MHz spectrometer), if the barrier ΔG^{*} were larger than 40 kJ mol^{-1}: J.A. Pople, W.G. Schneider and H.J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill, New York, 1959), p. 223. This line-broadening might be difficult to observe in our case, since only a small fraction of the complex is in the *cis* form. Therefore, this upper limit for ΔG^{*} must be regarded as tentative.