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Key indicators

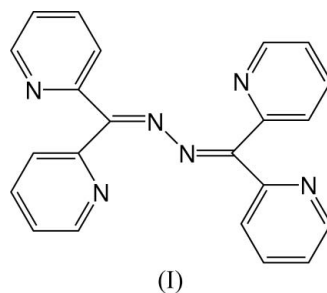
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.054
 wR factor = 0.169
Data-to-parameter ratio = 12.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Di-2-pyridyl ketone azine

In the crystal structure of the title compound, $\text{C}_{22}\text{H}_{16}\text{N}_6$, each molecule is disposed about a twofold axis perpendicular to the central N—N single bond. The two pyridyl rings bound to the same C atom make a dihedral angle of $73.40(9)^\circ$. The linkage C—N—N—C torsion angle is $-124.4(2)^\circ$.

Comment

Di-2-pyridyl ketone azine, (I), has been long associated with the spectrometric determination of microamounts of metal ions such as Cu^{II} (Grases, Estela *et al.*, 1981), Au^{III} (Grases, Garcia-Sanchez & Valcarcel, 1981), Pd^{II} (Garcia Vargas & Valcarcel, 1978), Fe^{II} (Valcarcel *et al.*, 1975), Ni^{II} and Co^{II} (Valcarcel *et al.*, 1977). A recent investigation of the coordination chemistry of this potential multidentate ligand suggests that (I) forms a discrete tetranuclear complex, (II), with AgNO_3 , while it decomposes on reaction with $\text{Cu}(\text{NO}_3)_2$ (Sumby & Steel, 2005). In the crystal structure of (II), there exist two discrete tetranuclear complexes within the asymmetric unit, each containing two molecules of ligand (I). As part of a further development of this project, we describe here the crystal structure of (I).



The title compound, (I), $\text{C}_{22}\text{H}_{16}\text{N}_6$, crystallizes in the monoclinic space group $P2_1/n$. The molecules of (I) are disposed about a twofold axis that is perpendicular to the central N—N single bond. Viewed along the twofold axis, all four pyridyl rings in the molecule are twisted in the same direction, showing a clockwise or anticlockwise configuration. Similar observations have also been reported in the tetranuclear silver(I) coordination complex (II). On the other hand, the flexible conformation of (I) makes it a potential hexadentate ligand capable of coordination *via* all its nitrogen donors (Sumby & Steel, 2005).

The geometry of the molecule of (I) differs from that of (II). The acute expression of the dihedral angle between the two pyridyl rings bonding to the same C atom is $73.40(9)^\circ$ in (I), while the corresponding values in (II) range from 66.3 to 81.3° , with an average of 72.1° (Sumby & Steel, 2005). For the free

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molecule of (I), the C–N–N–C torsion angle is $-124.4(2)^\circ$, while the four ligand molecules in (II) have values of $-138.0(5)$, $-149.4(5)$, $138.3(5)$ and $155.5(5)^\circ$, respectively. The N–N bond length at $1.371(4)$ Å for the molecule in (I) is also significantly shorter than those in (II), being 1.399 , 1.406 , 1.409 and 1.380 Å. These differences indicate that the ligand molecule (I) takes a more open conformation in its silver(I) coordination complex (II). Further investigation of the crystal packing of (I) indicates that no significant intermolecular interactions, such as hydrogen-bonding and π – π stacking, exist in this structure.

Experimental

Compound (I) was prepared according to the literature procedure (Sumbly & Steel, 2005). Single crystals suitable for X-ray diffraction were obtained by recrystallizing the polycrystalline powder sample from an ethyl acetate/hexane solution.

Crystal data

$C_{22}H_{16}N_6$	$D_x = 1.339$ Mg m $^{-3}$
$M_r = 364.41$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 581 reflections
$a = 12.226(4)$ Å	$\theta = 2.8$ – 21.3°
$b = 5.8241(19)$ Å	$\mu = 0.08$ mm $^{-1}$
$c = 13.617(4)$ Å	$T = 293(2)$ K
$\beta = 111.265(6)^\circ$	Block, colorless
$V = 903.6(5)$ Å 3	$0.32 \times 0.25 \times 0.18$ mm
$Z = 2$	

Data collection

Bruker APEXII CCD area-detector diffractometer	1597 independent reflections
φ and ω scans	1121 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.066$
$T_{min} = 0.919$, $T_{max} = 1.000$	$\theta_{max} = 25.0^\circ$
4795 measured reflections	$h = -12 \rightarrow 14$
	$k = -6 \rightarrow 6$
	$l = -16 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0836P)^2]$
$wR(F^2) = 0.169$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} < 0.001$
1597 reflections	$\Delta\rho_{max} = 0.35$ e Å $^{-3}$
127 parameters	$\Delta\rho_{min} = -0.28$ e Å $^{-3}$

All H atoms were placed in geometrically calculated positions, with C–H distances of 0.93 Å, and included in the final refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

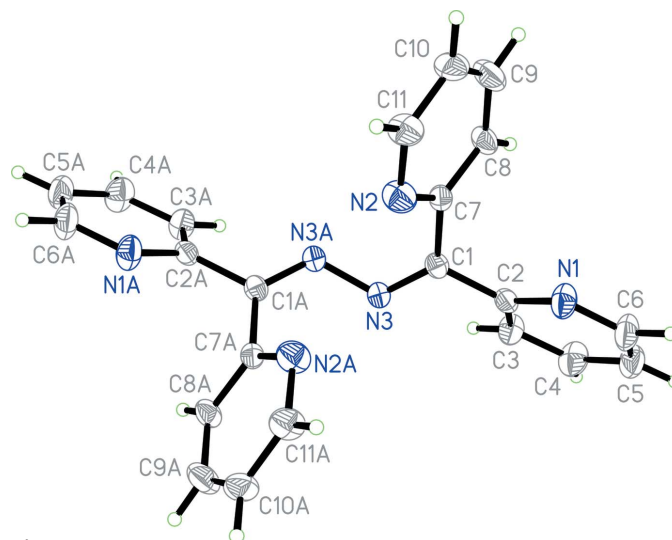


Figure 1
View of the molecular structure of (I), with the atom labeling and with 30% probability displacement ellipsoids (symmetry code: $\frac{1}{2} - x, y, \frac{3}{2} - z$).

Data collection: *APEXII* (Bruker, 2003); cell refinement: *APEXII* and *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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