18. Binuclear Copper(II) Complexes with *Robson*-Type Ligands. Synthesis, Characterization, Crystal Structure, and Magnetic Properties

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Three binuclear copper(II) complexes, $[Cu_2(\mu\text{-L})(\mu\text{-N}_3)](ClO_4)_2 \cdot 1.5$ EtOH (**1**), $[Cu_2(\mu\text{-L})(\mu\text{-MeO})(ClO_4)]$-$ClO_4 \cdot$ EtOH (**2**) and $[Cu_2(\mu\text{-L})(\mu\text{-C}_3H_3N_2)](ClO_4)_2 \cdot 2\,H_2O$, (**3**) where L is the pentadentale bridging ligand derived from 5-(*tert*-butyl)-2-hydroxybenzene-1,3-dicarbaldehyde bis(benzoylhydrazone) (HL) were synthesized and characterized. The crystal-structure determination of complex **2** provided the following crystal data: monoclinic, space group $P2_1/a$, $a = 11.412(2)$, $b = 24.509(4)$, $c = 14.833(4)$ Å, $\beta = 104.41(2)°$, $V = 4018(3)$ Å^3, $Z = 4$. The structure shows that the Cu^{II} ions are bridged by the endogenous phenolato O-atom and by an exogenous bridge CH_3O^-. The analysis of variable-temperature magnetic susceptibility data (4–300 K) indicates that there is an antiferromagnetic interaction between the Cu^{II} ions in these complexes with an exchange parameter ($2J$) of -119.1 cm^{-1} for complex **1** and -361.8 cm^{-1} for complex **3**. The effect of some exogenous bridging ligands on magnetic coupling for this type of complex is suggested.

Introduction. – The interest in μ-phenolato-bridged binuclear Cu^{II} complexes has risen sharply since the di-*Schiff* bases of 2,6-diformyl-4-methyl-phenol (= 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde) were first developed by *Robson* [1] in 1970. The so-called '*Robson*-type' ligands are predominantly noncyclic di-*Schiff* bases, derived mainly from 2,6-disubstituted phenols, thiophenols, and polyamines. They are known to be pentadentate and to form binuclear complexes bridged by the endogenous phenolato O-atom and exogenous groups (a variety of anions X$^-$). Following the initial work of *Robson* [1] [2], magnetic interactions in this type of complexes continue to be an area of research actively pursued by many groups [3–9]. Most of these studies focus on the magneto-structure correlation. The effect of endogenous bridges on the dissimilar-bridge systems is, however, poorly understood.

In recent papers, we have reported the magnetic properties of binuclear Cu^{II} complexes of 5-(*tert*-butyl)-2-hydroxybenzene-1,3-dicarbaldehyde bis(benzoylhydrazone) (= 2,6-diformyl-4-(*tert*-butyl)phenol di(benzoylhydrazone; HL)) with exogenous bromide [9a], chloride [9d], and ethanolato [9a] bridges. To study the effect of various exogenous bridges on the magnetic interaction, three new binuclear Cu^{II} complexes with the same ligand HL and the exogenous azide, methanolato, and 1*H*-pyrazol-1-yl bridges are reported here.

Experimental. – *General.* The 5-(*tert*-butyl)-2-hydroxybenzene-1,3-dicarbaldehyde was prepared according to [10]. All other chemicals were commercial anal. grade products and were used without further purification. Ligand HL was prepared as described previously [9a]. IR Spectra: KBr pellets, *IR-408* spectrometer. Molar conductances; *DDS-11A* conductometer. Thermogravimetric analyses: *Dupont* derivatograph, model *1090B*, with a heating rate of 5 min^{-1}. EPR Spectra: X-band *JES-FE1XG-EPR* spectrometer equipped with a 100 kHz field modulation unit; g values rel. to Mn(MgO). Magnetic Susceptibilities: the complexes were measured over the 4.2–300 K temp. range with a vibrating-sample magnetometer model *CF-1*; applied magnetic field 50 kG; diamagnetic corrections with *Pascal*'s constants [11] for all the constituent atoms; the effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$. Microanalyses: *Perkin-Elmer* elemental analyzer, model *240*.

$[Cu_2(\mu\text{-}L)(\mu\text{-}N_3)](ClO_4)_2 \cdot 1.5$ EtOH (**1**). A soln. of 5-(*tert*-butyl)-2-hydroxybenzene-1,3-dicarbaldehyde (0.5 mmol) and benzoylhydrazide (1 mmol) in EtOH (30 ml) was allowed to react with the EtOH soln. of copper(II) perchlorate hexahydrate (1 mmol) and NaN_3 (1 mmol). The soln. immediately turned dark green and a precipitate formed. After heating at *ca.* 60° for several hours, the mixture was allowed to stand at r.t. and then filtered. The green precipitate was washed with EtOH and dried in air. Anal. calc. for $C_{26}H_{25}Cl_2Cu_2N_7O_{11} \cdot 1.5\ C_2H_5OH$: C 39.64, H 3.87, N 11.16; found: C 39.88, H 3.54, N 11.25.

$[Cu_2(\mu\text{-}L)(\mu\text{-}MeO)(ClO_4)]ClO_4 \cdot$ EtOH (**2**). This complex was synthesized in MeOH using the same procedure as described for **1**, except for the addition of NaN_3. The resultant green powder was then recrystallized from EtOH. Serveral crystals suitable for X-ray single-crystal structure analyses were obtained.

$[Cu_2(\mu\text{-}L)(\mu\text{-}C_3H_3N_2)](ClO_4)_2 \cdot 2\ H_2O$ (**3**). This complex was obtained by a similar procedure as described for **1**, substituting 1*H*-pyrazole for NaN_3. Anal. calc. for $C_{29}H_{28}Cl_2Cu_2N_6O_{11} \cdot 2\ H_2O$: C 40.00, H 3.68, N 9.65; found: C 39.89, H 3.68, N 9.46.

X-Ray Diffraction Measurements. The crystal data and parameters of the data collection for complex **2** are given in *Table 1*. The structure was solved by direct methods using the program MULTAN 82. The Cu-atom positions were located in the initial E maps. The other non-H-atoms were determined with successive difference-*Fourier* syntheses. The final refinement by full-matrix least-squares with anisotropic thermal parameters for

Table 1. *Crystal Data and Parameters of Data Collection for Complex* **2**

Formula	$C_{29}H_{34}Cl_2Cu_2N_4O_{13}$
Formula weight	844.6
Crystal system	monoclinic
Space group	$P2_1/a$
a [Å]	11.412 (2)
b [Å]	24.509 (4)
c [Å]	14.833 (4)
α [°]	90
β [°]	104.41 (4)
γ [°]	90
V [Å^3]	4018 (3)
Z	4
D_c [$g \cdot cm^{-3}$]	1.51
Crystal dimensions [mm]	0.2 × 0.2 × 0.3
Temperature [K]	296 ± 1
Radiation (wavelength [Å])	MoK_α (0.71073)
Monochromator	graphite
Absorption correction applied	empirical[a])
Diffractometer	*Enraf-Nonius CAD$_4$*
Scan method	$\omega - 2\theta$
Scan width [°]	$2° < \theta < 23°$
Programs used	*Enraf-Nonius SDP-PLUS*
$F(000)$	1728
p-Factor used in weighting	1 for all observed reflections
Data collected	5897
Data with $I > 3\sigma(I)$	3816
R[b])	0.067
Rw[c])	0.073

[a]) See [12]. [b]) $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [c]) $Rw = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

non-H-atoms was converged with unweighted and weighted agreement factors of 0.067 and 0.073. The highest peak on the final difference-*Fourier* map was 0.78 e/Å^3. All data calculations were performed using the SDP-PLUS program system.

Results and Discussion. – *Composition of the Complexes.* The elemental-analysis data are consistent with the general formula $[Cu_2(\mu\text{-L})(\mu\text{-X})]^{2+}$ for complexes **1** and **3**. Their molar conductivities fall into the expected range for 1:2 electrolytes, indicating that the perchlorate anions are outside the coordination sphere. Thermogravimetric analyses show a weight loss corresponding to the elimination of 1.5 EtOH molecules for complex **1** at *ca.* 83° and 2 H_2O molecules for complex **3** in the temperature range 75–115° per binuclear unit. Thus, the complexes are proposed to have a μ-phenolato bridge and a μ-X bridge structure, and the Cu^{II} ion is in a distorted square-planar environment.

IR Spectra. The free ligand HL shows two sharp IR bands at 1650 and 1540 cm^{-1}, attributable to the C=O and C=N stretching vibration. The $\tilde{\nu}$(C=O) bands shift to 1610–1620 cm^{-1} and the $\tilde{\nu}$(C=N) bands to 1550–1575 cm^{-1} on formation of complexes. The hydrazone $\tilde{\nu}$(NH) absorption, in the free ligand at 3100 cm^{-1}, is observed at 3150–3180 cm^{-1} for the three complexes. In addition, the complexes show a broad band at *ca.* 1030–1095 cm^{-1} which should be assigned to $\tilde{\nu}(ClO_4^-)$ absorptions.

The only known modes of azide bridging involve coordination either through a single N-atom as in the 1,1-N_3 mode or through the two terminal N-atoms as in the 1,3-N_3 mode. *Nelson* and *Nelson* have concluded that the $\tilde{\nu}$s frequency can be used to distinguish between the 1,1-N_3 mode and the 1,3-N_3 mode [13]. The appearance of a band of medium intensity near 1300 cm^{-1}, ascribed to $\tilde{\nu}$s, indicates the presence of a bridging azide as in the 1,1-N_3 mode, whereas for the 1,3-N_3 mode, in which the azide fragment is much more symmetrically bound, $\tilde{\nu}$s is IR-inactive or, at best, very weak. A band of medium intensity at 1300 cm^{-1} is observed in the azide-bridged complex **1** reported here, with the sharp band at 2080 cm^{-1} attributable to the $\tilde{\nu}_{as}(N_3)$ stretching frequency. This strongly supports the azide bridging mode through a single N-atom in complex **1**.

For complex **3**, a medium-intensity band appears at 1635 cm^{-1}, characteristic of a bidentate-bridged pyrazolyl group [2a].

Crystal Structure of Complex **2**. The ORTEP drawing of $[Cu_2(\mu\text{-L})(\mu\text{-MeO})(ClO_4)]^+$ with the atom-numbering scheme is shown in *Fig. 1*. Selected bond distances and angles with their estimated standard deviations are listed in *Table 2*. The structure of **2** shows that both Cu-atoms of the binuclear unit are connected by an endogenous phenolato O-atom O(1) and an exogenous methoxy O-atom O. The coordination geometries of Cu(1) and Cu(2) are different, Cu(1) is five-coordinate with a square-pyramidyl coordination geometry, whilst Cu(2) is four-coordinate with a square-planar geometry. The axial coordination site of Cu(1) is occupied by a perchlorate group, and the Cu(1)–O(22) distance is 2.283(5) Å. The deviation of Cu(1) from the coordinate plane (the least-squares plane composed of O(1), O(2), N(1), and O) is 0.124 Å, while Cu(2) lies 0.012 Å below the coordinate plane (the least-squares plane composed of O(1), O(3), N(3), and O). The dihedral angle between the coordinate planes in the binuclear unit is 11.72°. The Cu(1)–O(1)–Cu(2) and Cu(1)–O–Cu(2) angles of the Cu_2O_2 core consisting of Cu(1), Cu(2), O(1), and O are 96.5(1) and 96.6(1)°, respectively. This core structure is very similar with the ethanolato-bridged binuclear copper(II) complex $[Cu_2(\mu\text{-L})(\mu\text{-EtO})(MeOH)](ClO_4)_2$ which was described earlier [9a].

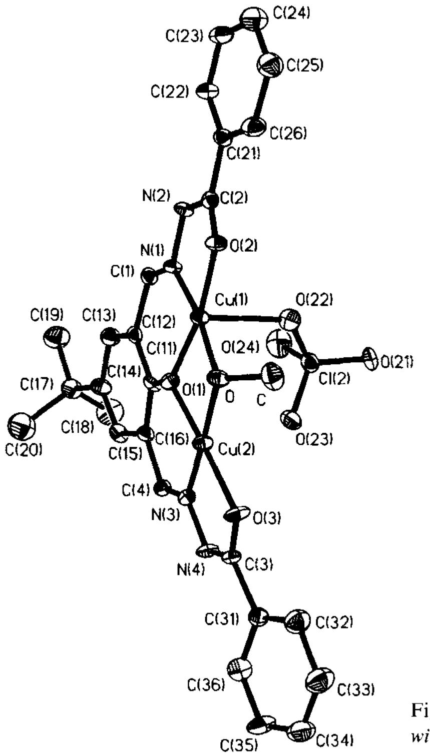

Fig. 1. *ORTEP View of complex* **2** *with the atom numbering scheme*

Table 2. *Selected Bond Distances* [Å] *and Angles* [°] *of Complex* **2**

Cu(1)–O(1)	1.924(3)	O(1)–Cu(2)–O	82.2(1)
Cu(1)–O(2)	1.962(3)	O(3)–Cu(2)–N(3)	82.4(1)
Cu(1)–N(1)	1.936(3)	O(3)–Cu(2)–O	104.3(1)
Cu(1)–O	1.930(3)	N(3)–Cu(2)–O	173.1(1)
Cu(2)–O(1)	1.932(3)	Cu(1)–O(1)–C(11)	131.3(3)
Cu(2)–O(3)	1.958(3)	Cu(2)–O(1)–C(11)	130.2(3)
Cu(2)–N(3)	1.929(4)	Cu(1)–O(2)–C(2)	112.8(3)
Cu(2)–O	1.925(3)	Cu(2)–O(3)–C(3)	111.6(3)
Cu(1)–O(22)	2.283(5)	Cu(1)–N(1)–N(2)	110.5(2)
O(1)–Cu(1)–O(2)	168.6(1)	Cu(1)–N(1)–C(1)	129.3(4)
O(1)–Cu(1)–N(1)	90.0(1)	Cu(2)–N(3)–N(4)	110.7(3)
O(1)–Cu(1)–O	82.3(1)	Cu(2)–N(3)–C(4)	130.7(4)
O(2)–Cu(1)–N(1)	81.9(1)	Cu(1)–O–Cu(2)	96.6(1)
O(2)–Cu(1)–O	105.0(1)	Cu(1)–O–C	121.0(3)
N(1)–Cu(1)–O	170.4(1)	Cu(2)–O–C	119.1(3)
O(1)–Cu(2)–O(3)	173.5(1)	Cu(1)–O(1)–Cu(2)	96.5(1)
O(1)–Cu(2)–N(3)	91.1(1)		

Electron Paramagnetic Resonance. The X-band EPR spectra of powdered samples of three complexes at both room-temperature and 140 K have been recorded. All of the room-temperature spectra show a rather atypical pattern with a central signal at *ca.* 3500 G and a relatively weak half-field absorption at *ca.* 1800 G. The central signal can be tentatively assigned to the overlap of the $\Delta Ms = 1$ transition of coupled Cu^{II} ions and uncoupled Cu^{II} signals, and the half-field signals should be assigned to the $\Delta Ms = 2$ transition. The apparent half-field signals are expected for the magnetically coupled dinuclear Cu^{II} complexes. The intensitive of coupled Cu^{II} signals of complexes decrease and the signals of uncoupled Cu^{II} ions increase upon cooling to 140 K, indicating that an antiferromagnetic coupling operates in the complexes, which is in agreement with the results of the magnetic investigation as discussed below.

Magnetic Properties. The variable-temperature susceptibility of complexes **1** and **3** were recorded in the 4.2–300 K region. The observed magnetic moments for each binuclear unit at room temperature are $2.08\mu_B$ (295 K) for complex **1** and $1.82\mu_B$ (294 K) for complex **3**, which are considerably less than the spin-only value (2.45 μ_B). This suggests the operation of an intramolecular antiferromagnetic interaction. The magnetic susceptibility data for complexes **1** and **3** are plotted in *Fig. 2*. To understand quantitatively the magnitudes of spin-exchange interaction, the magnetic data were analyzed with the *Bleaney-Bowers* equation (*Eqn. 1*) based on the *Heisenberg* model ($H = -2JS_1S_2$, $S_1 = S_2 = \frac{1}{2}$) [14]:

$$\chi = \frac{2N\beta^2g^2}{kT}[3 + \exp(-2J/kT)]^{-1}(1 - \rho) + \frac{N\beta^2g^2}{2kT}\rho + TIP \qquad (1)$$

where χ denotes the susceptibility per binuclear complex and $2J$ represent the singlet-triplet energy gap. In addition, the data were corrected for the presence of a small proportion ρ of uncoupled Cu^{II} and the temperature-independent paramagnetism (*TIP*) of the Cu^{II} ions. The other symbols have their usual meaning. As shown in *Fig. 2*, good least-squares fit to the experimental data is attained with *Eqn. 1*. The best-fit parameters for complex **1** are $2J = -119.1$ cm^{-1}, $g = 2.12$, $\rho = 0.022$, $TIP = 120 \cdot 10^{-6}$ cgs·mol^{-1}, and $R = 1.0 \cdot 10^{-5}$, and for complex **3**, $2J = -361.8$ cm^{-1}, $g = 2.11$, $\rho = 0.032$, $TIP = 120 \cdot 10^{-6}$ cgs·mol^{-1}, and $R = 2.7 \cdot 10^{-5}$. The agreement factor R is defined here as $\Sigma(\chi^{obs} - \chi^{calc})^2/\chi^{obs}$.

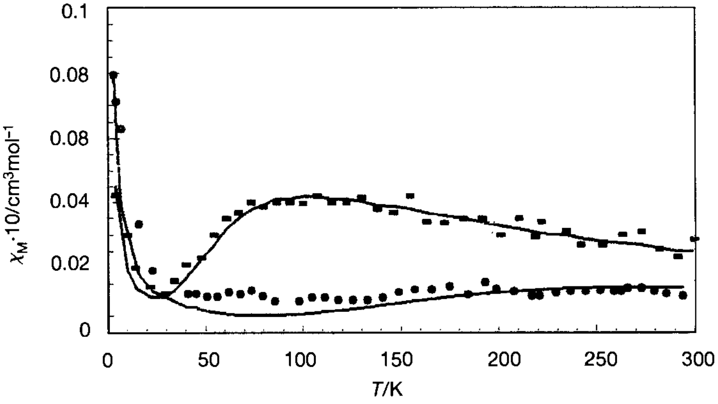

Fig. 2. *Temperature dependence of magnetic susceptibility χ for complexes* **1** (■) *and* **3** (●). The solid lines show the best fit to the data using the parameters and equation described in the text.

For complex **2**, unfortunately, the amount of single crystals is too small to use it in magnetic measurements. However, comparing the crystal structure of complex **2** with that of the ethanolato-bridged binuclear Cu^{II} complex [Cu_2(μ-L)(μ-EtO)(MeOH)](ClO_4)$_2$ [9a] in detail reveals that the structural parameters related to the magnetic properties are very close. In both complexes, Cu(1) is five-coordinate with a square-pyramidal coordination geometry, whilst Cu(2) is four-coordinate with a square-planar geometry. The only difference is that in the MeO-bridged complex **2**, the perchlorate group, instead of the MeOH molecule in the EtO-bridged complex, occupies the axial coordination site of Cu(1). The Cu–O(phenolato)–Cu angles of the Cu_2O_2 core consisting of Cu(1), Cu(2), and the phenolato and exogenous O-atoms (EtO or MeO) are 96.5(1) and 96.2(3)°, respectively. The dihedral angle between the coordinate planes containing Cu(1) and Cu(2) in the binuclear unit are 8.51° for the EtO-bridged complex and 11.72° for the MeO-bridged complex. In addition, the EtO and MeO group have similar electronegativities when they are in equivalent bridging configurations. Therefore, from the similarity of details, *i.e.*, the coordination environment of Cu^{II} ions, the Cu_2O_2 network, and the electronegativity of exogenous bridges, we deduce that the spin-exchange interaction of complex **2** is also similar to that of the EtO bridged binuclear complex [15].

The magnetic interaction of binuclear Cu^{II} complexes of 5-(*tert*-butyl)-2-hydroxybenzene-1,3-dicarbaldehyde bis(benzoylhydrazone) with bromide [9a], chloride [9d], and ethanolato [9a] exogenous bridges has been reported, and the singlet-triplet separations ($2J$) were -47.8 (Br^--bridged), -57.6 (Cl^--bridged) and -308.7 cm^{-1} (EtO^--bridged), respectively. These complexes exhibit an antiferromagnetic coupling, the magnitude of which strongly depends on the nature of the exogenous bridging ligand. It was observed that $-2J$ (cm^{-1}) decreases in the order: $C_3H_3N_2^-$ (361.8) > EtO^- (308.7) > 1,1-N_3^- (119.1) > Cl^- (57.1) > Br^- (47.8). The strongest antiferromagnetic coupling of this series is observed in the pyrazolyl-bridged binuclear complexes (*e.g.* **3**). This can be rationalized by the orbital complementary effect [16–18] derived from the *Hoffmann* theory [19]. Meanwhile, 1*H*-pyrazolyl is a bidentate conjugate ligand. The Cu–O(phenolato)–Cu angle is larger than that of other complexes, and the extent of the coordination plane is high, which favors the electron transfer [15]. For ethanolato- and 1,1-azide-bridged binuclear complexes the stronger antiferromagnetic couplings are expected, according to the symmetry of their HOMO [5c, d] [20]. However, the antiferromagnetic coupling of the 1,1-azide-bridged binuclear complex **1** is considerably smaller than that of the ethanolato-bridged complex. The reason for this is mainly due to the spin-polarization effect of the N_3^- ion proposed by *Kahn* and coworkers [21]. Since the electronegativity is large and the electron density on halide bridges is low, the overlap integrals between magnetic orbitals are small and lead to the relatively small value of $-2J$. A stronger antiferromagnetic coupling of the chloride-bridged complex is observed in comparison with the bromide-bridged complex. As shown by *Güdel* and coworkers, a theoretical analysis predicts a more efficient overlap integral for Cl^- when Cl^- and Br^- are in equivalent bridging configurations [22]. Therefore, the larger antiferromagnetic coupling exhibited by the chloride-bridged relative to that of the bromide-bridged complex is expected.

It should be emphasized that the sequence of the effect of some exogenous bridging ligands on magnetic coupling corresponds to that in spectra-chemical series. In *Table 3*, we have listed the summary of $2J$ values for some binuclear Cu^{II} complexes with different exogenous bridging ligands. From this limited set of complexes as well as from theoretical analyses [4] [5] [9], we can deduce a relationship between magnetism and spectro-chemical series for this type of complexes. Studies focusing on the structural details and theoretical calculation of these complexes are in progress.

Table 3. *Summary of* $2J$ [cm^{-1}] *Values for Some Binuclear Complexes with Different Exogenous Bridging Ligands*

Binucleating ligand	Exogenous bridging ligand						Ref.
	Br^-	Cl^-	1,1-N_3^-	EtO^-	HO^-	$C_3H_3N_2^-$	
L^3[a])		−230			−385		[6]
$Famp^-$[b])	−68	−84			−364		[4a,b]
$Fdmen^-$[c])	−157		−86		−367		[5b] [4c]
H_2L'[d])	−6	−76	−87	−231	−242	−344	[9c,f]
L'[e])		−123	−177		−325	−410	[9e]
HL	−48	−57	−119	−309		−361	this work

[a]) L^3 = monoanion (phenolate) of 4-methyl-2,6-bis[*N*-(2-pyridylethyl)formimidoyl]phenol (= 2-hydroxy-5-methyl-*N*,*N'*-bis[2-(pyridin-2-yl)ethyl]benzene-1,3-dimethanimine).

[b]) $Famp^-$ = monoanion (phenolate) of 2,6-bis[*N*-(2-pyridylmethyl)formimidoyl]-4-methylphenol (= 2-hydroxy-5-methyl-*N*,*N'*-bis[(pyridin-2-yl)methyl]benzene-1,3-dimethanimine).

[c]) $Fdmen^-$ = ligand derived from the condensation of 2,6-diformyl-4-methylophenol (= 2-hydroxy-5-methylbenzene-1,3-dicarboxaldehyde) and 1,1-methylenediamine.

[d]) H_2L' = monoanion (phenolate) of 2,6-diformyl-4-methylphenol bis(benzoylhydrazone).

[e]) L' = trianion (phenolate and two enolate groups (NH=C−O)) of 2,6-diformyl-4-methylphenol bis(benzoylhydrazone).

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