

Emission Energy Correlates with Inverse of Gold–Gold Distance for Various $[\text{Au}(\text{SCN})_2]^-$ Salts

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Luminescence of gold(I) compounds in the solid state has received considerable study.^{1,2} The aurophilic interaction to form gold–gold dimers, trimers, and infinite chains is known to be intimately involved as a source of the observed emissions; however, generally, the luminescence energy is not correlated with the gold–gold distance.^{3,4} This could well result from the changes which occur in ligating atom or ligand type as well as changes in gold–gold distance in many of the studies.

We have synthesized a series of salts of the bis(thiocyanato)aurate(I) anion, including the following counterions: K^+ , Rb^+ , Cs^+ , Me_4N^+ , $[(n\text{-Bu})_4\text{N}]^+$, and Ph_4P^+ . Generally, the compounds have been synthesized by reaction of 2 equiv of the thiocyanate salt of the desired cation with chlorogold(I)tetrahydrothiophene⁵ in acetonitrile. The metal chloride formed is nearly insoluble and may be filtered off. X-ray quality crystals were generally obtained by dissolution in acetonitrile followed by ether vapor diffusion at 4 °C. Each of these materials was characterized by negative ion FT-ICR MS which showed the bis(thiocyanato)aurate ion as the principal peak. The compounds were characterized by IR, Raman, and UV–visible spectroscopies. Representative spectra for the K^+ species are shown in the Supporting Information. All compounds have similar spectra, except for the tetraphenylphosphonium salt where the benzene moieties make obvious contributions. The nature of the cation was determined by the syntheses and confirmed by proper fits to atomic number and ion structure in the crystal structures.

The single-crystal X-ray structures of each salt have been determined.⁶ The structures fall into three classes. The phosphonium salt contains isolated monomers with an Au–S–C angle of 101.2° and a pure trans configuration of the thiocyanate ligands. The alkali salts are nearly isostructural, consisting of infinite linear chains with alternating short and long gold–gold bond distances along the chain. The $[\text{Me}_4\text{N}]^+$ salt forms a kinked chain of trimers joined at a shared gold atom as the kink. They have the pattern of short–short/long–long Au–Au bonds. Finally, the $[(n\text{-Bu})_4\text{N}]^+$ salt contains isolated dimers with relatively short, 3.07 Å Au–Au distances. Figure 1 shows, as an example, the structure of the short Au–Au dimer portion of the K^+ salt.

All of the materials with gold–gold bonds emit as polycrystalline specimens at 77 K with λ_{max} ranging from 506 to 670 nm. Table 1 lists the observed gold–gold distances and the energy of the emission maximum for each structure. Note that both the short and long Au–Au distances are listed for the infinite chain structures. Figure 2 shows the shift in emission versus the short gold–gold interactions.⁷ Fackler, Schmidbauer, and co-workers⁸ suggested that emission should correlate inversely with distance. Figure 3 shows a plot of emission energy (cm^{-1}) versus the reciprocal of the short Au–Au distances (\AA^{-1}). There appears to be a relatively strong correlation between the two. Interestingly, the point for Rb^+ , which by eye appears to give the poorest correlation, has little effect on the results sought. The important aspect is the slope of the line,

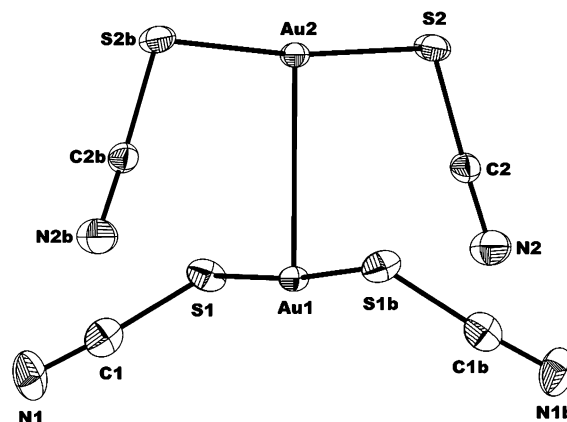


Figure 1. Ortep drawing of $\{\text{K}[\text{Au}(\text{SCN})_2]\}_n$ dimeric portion.

Table 1. Au–Au Bond Distances (Å), Excitation and Emission Wavelengths (nm), and Energy (cm^{-1})^a

	Au–Au (Å)	excitation	emission	energy
K^+	3.0064(5)	320	516	19 379
	3.0430(5)			
$[(n\text{-Bu})_4\text{N}]^+$	3.0700(8)	360	539	18 552
	3.0821(4)			
Rb^+	3.1144(5)	325	635	15 748
	3.1794(2)			
Cs^+	3.2654(2)	320	670	14 925
	3.2128(11)			
Na^{\ominus}	3.2399(11)	320	710	14 084

^a X-ray data for the Rb^+ and Cs^+ salts were collected at 170 K; all others were collected at 150 K.

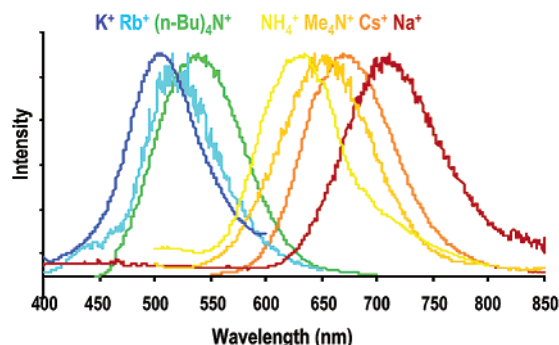


Figure 2. Emission spectra of oligomeric salts of $[\text{Au}(\text{SCN})_2]^-$ at 77 K.

i.e., the shift in wavelength as a function of bond length, and inclusion of the Rb^+ point has little bearing on the slope.⁹ Length appears not to be a factor as the dimeric $[(n\text{-Bu})_4\text{N}]^+$ salt falls close to the line of the infinite chain alkali salts. Also, the trimeric $[\text{Me}_4\text{N}]^+$ salt with two adjacent 3.18 Å short distances falls on the same line. Finally, cation size is not determinative of the emission

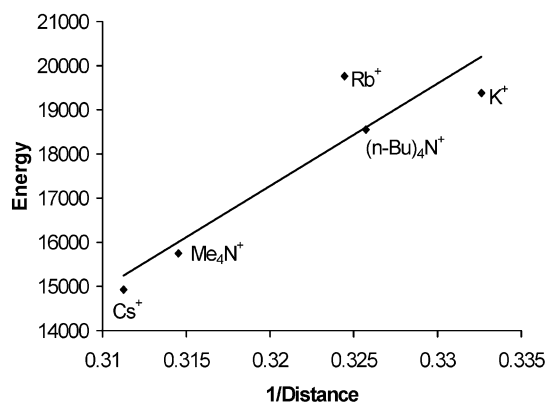


Figure 3. Energy (cm^{-1}) versus $1/d$ (\AA^{-1}) of the short Au–Au interaction of $[\text{Au}(\text{SCN})_2]_n$.⁷

energy, which would be expected to have the trend K^+ , Rb^+ , Cs^+ , Me_4N^+ , and $[(n\text{-Bu})_4\text{N}]^+$ in contrast to the observed order.

A remarkable series of conclusions can be drawn, however. First, given the isolated dimers in the $[(n\text{-Bu})_4\text{N}]^+$ salt, a single gold–gold pair must serve as the emissive source. Second, the trimeric group of gold atoms of equal distance behaves as though a single pair is the emissive source. Third, extending the chain to infinity, by a series of short/long links again suggests that a single gold–gold pair serves as the emissive source.

Further studies of the K^+ salt, in collaboration with others,¹⁰ at temperatures approaching 4 K indicate a second emission band with a shorter lifetime arises at a shorter wavelength. A detailed report will follow.

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Supporting Information Available: X-ray crystallographic data in text format, figures showing the structure of each complex and packing diagram, and tables for all complexes, spectroscopic, and photophysical data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- $\{\text{K}[\text{Au}(\text{SCN})_2]\}_n$, 1, X-ray data were collected at 150 K on a SMART 1K CCD (Mo $\text{K}\alpha$). Structure solutions were obtained by standard Patterson and difference Fourier methods and refined on F^2 . $a = 13.1181(10)$ \AA , $b = 6.0494(5)$ \AA , $c = 17.7732(14)$ \AA , $\alpha = 90^\circ$, $\beta = 110.3870(10)^\circ$, $\gamma = 90^\circ$, $V = 1322.07(18)$ \AA^3 , monoclinic $C2/c$, $Z = 4$, $\theta_{\text{min}/\text{max}} = 3.31/29.45^\circ$, 1257 [$I > 2\sigma(I)$] unique observed reflections were used to refine 74 variable parameters and gave a final R factor of 0.0376. $\{\text{Rb}[\text{Au}(\text{SCN})_2]\}_n$, 2, X-ray data were collected at 173 K on a Kappa goniostat with a SMART6000 CCD detector at ChemMatCARS using synchrotron radiation tuned to Ag $\text{K}\alpha$ radiation, $\lambda = 0.55940$ \AA . Structure solutions were obtained by direct methods and difference Fourier methods and refined on F^2 . $a = 13.0814(2)$ \AA , $b = 6.1965(6)$ \AA , $c = 17.6736(2)$ \AA , $\alpha = 90^\circ$, $\beta = 108.536(4)^\circ$, $\gamma = 90^\circ$, $V = 1358.3(3)$ \AA^3 , monoclinic $C2/c$, $Z = 4$, $\theta_{\text{min}/\text{max}} = 2.59/21.92^\circ$, 1335 [$I > 2\sigma(I)$] unique observed reflections were used to refine 74 variable parameters and gave a final R factor of 0.0376. $\{\text{Cs}[\text{Au}(\text{SCN})_2]\}_n$, 3, X-ray data were collected at 173 K on a Kappa goniostat with a SMART6000 CCD detector at ChemMatCARS using synchrotron radiation tuned to Ag $\text{K}\alpha$ radiation, $\lambda = 0.55940$ \AA . Structure solutions were obtained by direct methods and difference Fourier methods and refined on F^2 . $a = 13.1550(1)$ \AA , $b = 6.4417(9)$ \AA , $c = 17.790(2)$ \AA , $\alpha = 90^\circ$, $\beta = 107.229(6)^\circ$, $\gamma = 90^\circ$, $V = 1439.9(3)$ \AA^3 , monoclinic $C2/c$, $Z = 4$, $\theta_{\text{min}/\text{max}} = 2.80/16.26^\circ$, 649 [$I > 2\sigma(I)$] unique observed reflections were used to refine 74 variable parameters and gave a final R factor of 0.0309. $\{\text{Me}_4\text{N}[\text{Au}(\text{SCN})_2]\}_n$, 4, X-ray data were collected at 150 K on a SMART 1K CCD (Mo $\text{K}\alpha$). Structure solutions were obtained by direct methods and difference Fourier methods and refined on F^2 . $a = 12.6423(3)$ \AA , $b = 9.6723(2)$ \AA , $c = 19.0040(6)$ \AA , $\alpha = 90^\circ$, $\beta = 105.357(1)^\circ$, $\gamma = 90^\circ$, $V = 2240.84(10)$ \AA^3 , monoclinic $P2_1/c$, $Z = 4$, $\theta_{\text{min}/\text{max}} = 1.67/28.28^\circ$, 4710 [$I > 2\sigma(I)$] unique observed reflections were used to refine 220 variable parameters and gave a final R factor of 0.0410. $[(n\text{-Bu})_4\text{N}]_2\text{[Au}_2(\text{SCN})_4]$, 5, X-ray data were collected at 150 K on a SMART 1K CCD (Mo $\text{K}\alpha$). Structure solutions were obtained by direct methods and difference Fourier methods and refined on F^2 . $a = 12.512(3)$ \AA , $b = 28.964(8)$ \AA , $c = 12.898(3)$ \AA , $\alpha = 90^\circ$, $\beta = 93.014(2)^\circ$, $\gamma = 90^\circ$, $V = 4667.9(19)$ \AA^3 , monoclinic $P2_1/n$, $Z = 4$, $\theta_{\text{min}/\text{max}} = 2.62/26.37^\circ$, 5151 [$I > 2\sigma(I)$] unique observed reflections were used to refine 427 variable parameters and gave a final R factor of 0.0410. $[\text{Ph}_4\text{P}][\text{Au}(\text{SCN})_2]$, 6, X-ray data were collected at 292 K on a SMART 1K CCD (Mo $\text{K}\alpha$). Structure solutions were obtained by direct methods and difference Fourier methods and refined on F^2 . $a = 16.699(2)$ \AA , $b = 7.3184(9)$ \AA , $c = 22.002(3)$ \AA , $\alpha = 90^\circ$, $\beta = 111.913(3)^\circ$, $\gamma = 90^\circ$, $V = 2494.6(5)$ \AA^3 , monoclinic $C2/c$, $Z = 4$, $\theta_{\text{min}/\text{max}} = 2.63/28.29^\circ$, 1854 [$I > 2\sigma(I)$] unique observed reflections were used to refine 148 variable parameters and gave a final R factor of 0.0519.
- The excitation wavelengths used for the emission of Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Me_4N^+ , and $(n\text{-Bu})_4\text{N}^+$ are 320, 320, 320, 320, 360, 325, and 360 nm, respectively.
- Assefa, Z.; McBurnett, B.; Staples, R.; Fackler, J. P., Jr.; Assmann, B.; Angermaier, K.; Schmidbaur, H. *Inorg. Chem.* **1995**, *34*, 75–83. Figures with plots of distance or reciprocal distance are of essentially equal correlation merit (distance plot $R^2 = 0.8563$, reciprocal distance $R^2 = 0.8464$).
- The R^2 value for the five-point correlation of Figure 3 is 0.85 with a slope of -24.0 ± 1.85 $\text{K cm}^{-1}/\text{\AA}$, with the results for the Rb^+ appearing to be an outlier. With this last point removed, the R^2 for the four-point correlation is 0.986 with a slope of -22.3 ± 1.85 $\text{K cm}^{-1}/\text{\AA}$. Statistically, the slopes are equivalent, although by means of a t test one can reject the Rb^+ datum at the 99.5% confidence level. Using statistical tests to reject data with such a small set of points is problematic, but with or without the Rb^+ datum there appears to be a clear linear relationship between the inverse of metal center distances and the emission energies for the compounds studied.
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